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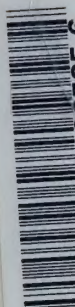
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Technical

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Spills

BENZENE

March 1984

Canada

ENVIRONMENTAL TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

BENZENE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario



March 1984

FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The Canadian Chemical Producers' Association is especially acknowledged for its review of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.



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1 SUMMARY

BENZENE (C₆H₆)

Colourless liquid with a gasoline-like odour

SYNONYMS

Benzole, Benzol, Phene, Benzin, Benzine, Benzolene, Bicarburet of Hydrogen, Carbon Oil, Coal Naphtha, Cyclohexatriene, Mineral Naphtha, Motor Benzol, Nitration Benzene, Phenyl Hydride, Pyrobenzol

IDENTIFICATION NUMBERS

UN. No. 1114; CAS No. 71-43-2; OHM-TADS No. 7616601; STCC No. 4908110

GRADES & PURITIES

Nitration grade, minimum 99 percent

IMMEDIATE CONCERNS

Fire: Flammable liquid. Vapour forms explosive mixtures with air. Flashback may occur along vapour trail

Human Health: Toxic via inhalation, ingestion, and skin contact; a human carcinogen

Environment: Toxic to aquatic life. Harmful to some species at concentrations as low as 5 mg/L

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): liquid

Boiling Point: 80.1°C

Melting Point: 5.5°C

Flammability: flammable

Flash Point: -11°C (CC)

Specific Gravity (water=1): 0.879 (20°/20°C)

Vapour Pressure: 10.1 kPa @ 20°C

Solubility (in water): 0.18 g/100 g (25°C)

Behaviour (in water): floats on water, no reaction

Behaviour (in air): vapour forms explosive mixtures with air

Odour Threshold: 2 to 5 ppm

ENVIRONMENTAL CONCERNS

Benzene is toxic to aquatic life. It is hazardous to waterfowl and animals. Benzene may be bioaccumulative in living organisms, but has no food chain concentration potential. There is a cycling of benzene between the atmosphere and water.

HUMAN HEALTH

TLV*: 10 ppm (30 mg/m³) (skin)

IDLH: 2000 ppm

Carcinogen

Exposure Effects

Inhalation: Inhalation of vapour causes headache, confusion, nausea, difficult breathing, collapse, bronchitis and pneumonia. Effects are cumulative

Contact: Prolonged skin exposure causes irritation and symptoms as found for inhalation. Eye contact yields irritation from liquid or high vapour concentrations

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "FLAMMABLE". Call fire department and notify manufacturer. Eliminate sources of ignition including traffic and equipment. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Use foam, dry chemical or carbon dioxide to extinguish. Do not extinguish fire unless release is stopped. Cool fire-exposed containers with water. Stay clear of ends of tanks.

COUNTERMEASURES

Emergency Control Procedures in/on:

Soil: Construct barriers to contain spill or divert to impermeable surfaces. Remove material with pumps or vacuum equipment. Absorb residual liquid on natural or synthetic sorbents, shovel into metal containers which can be covered

Water: Contain with booms, weirs or natural barriers. Use (oil) skimming equipment or suction hoses to remove slick, followed by the application of sorbents. Equipment should be explosion-proof

Air: Use water spray to knock down and disperse flammable vapour. Control runoff for later treatment and/or disposal

NAS HAZARD RATING

<u>Category</u>	<u>Rating</u>
Fire.....	3
Health	
Vapour Irritant.....	1
Liquid or Solid Irritant.....	1
Poison.....	3
Water Pollution	
Human Toxicity.....	1
Aquatic Toxicity.....	3
Aesthetic Effect.....	2
Reactivity	
Other Chemicals.....	1
Water.....	0
Self-reaction.....	0

NFPA
HAZARD
CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Colourless liquid (Dow ERIS 1981)
Usual shipping state	Liquid above 10°C (Dow ERIS 1981)
Physical state at 15°C, 1 atm	Liquid (Dow ERIS 1981)
Melting point	5.53°C (Cheremisinoff 1979)
Boiling point	80.1°C (Cheremisinoff 1979)
Vapour pressure	13.33 kPa (26°C) (Kirk-Othmer 1978) 10.1 kPa (20°C) (Cheremisinoff 1979)

Densities

Density	873.7 kg/m ³ (-4°C) (Kirk-Othmer 1978)
Specific gravity	0.879 (20°/20°C) (Cheremisinoff 1979) 4.0 (vapour at 90°C) (Cheremisinoff 1979) 2.77 (vapour at 20°C) (Verschuere 1977)

Fire Properties

Flammability	Flammable liquid (NFPA 1978)
Flash point, CC	-11°C (NFPA 1978)
Autoignition temperature	498°C (NFPA 1978)
Burning rate	6.0 mm/min (CHRIS 1978)
Upper flammability limit, UFL	7.1 percent (NFPA 1978)
Lower flammability limit, LFL	1.3 percent (NFPA 1978)
Flame speed	0.40 m/s (maximum) (Cheremisinoff 1979)
Burning characteristics	Burns with a smokey flame (CCD 1977)
Heat of combustion	41.8 kJ/g (25°C) (Kirk-Othmer 1978)
Combustion products	Water, carbon dioxide and carbon monoxide
Flashback potential	Vapour may travel considerable distance to a source of ignition and flash back (NFPA 1978)
Explosiveness	Vapours form explosive mixtures with air at 1.3 to 7.1 percent (NFPA 1978)
Electrical ignition hazard	May be ignited by static discharge

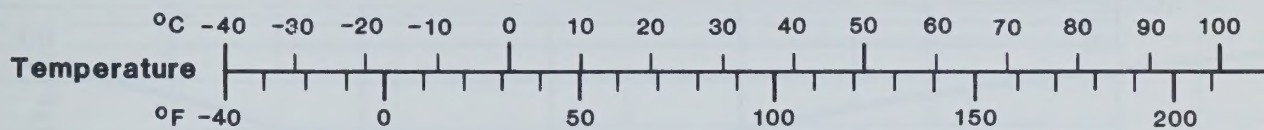
Other Properties

Molecular weight of pure substance	78.12 (CRC 1980)
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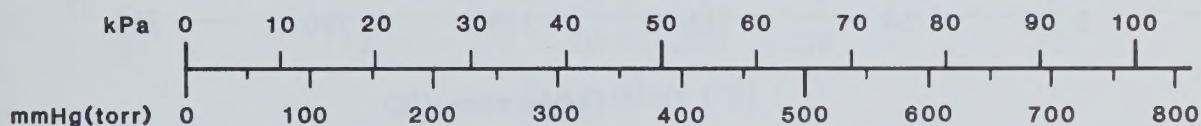
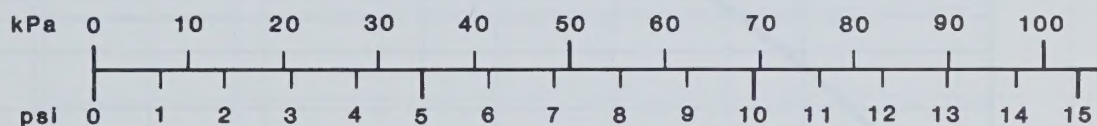
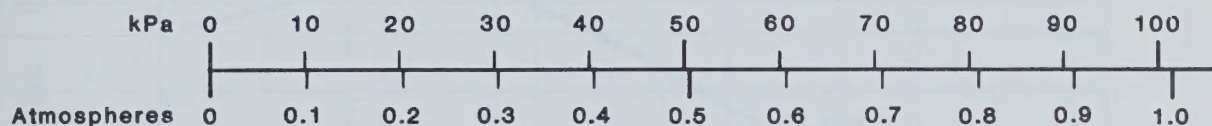
Constituent components of typical commercial grade	99 percent benzene 0.1 percent toluene 0.5 percent non-aromatics (Texaco MSDS)
Refractive index	1.5011 (CRC 1980)
Viscosity	0.6468 mPa·s (20°C) (Cheremisinoff 1979)
Interfacial tension with air	28.12 mN/m (25°C) (Kirk-Othmer 1978)
Interfacial tension with water	35 mN/m (20°C) (CRC 1980)
Hygroscopicity	Maximum moisture absorbed, < 0.1 percent (MCA 1960)
Latent heat of fusion	9.850 kJ/kg-mole (5.5°C) (Kirk-Othmer 1978)
Latent heat of sublimation	33.8 kJ/kg-mole (25°C) (Lange's Handbook 1979)
Latent heat of vaporization	33.87 kJ/kg-mole (80.1°C) (Kirk-Othmer 1978)
Heat of formation	49.0 kJ/mole (25°C) (Sussex 1977)
Ionization potential	9.25 eV (Rosenstock 1977)
Heat capacity	
constant pressure (C_p)	135 J/(g-mole·°C) (25°C) (CRC 1980)
constant volume (C_v)	127 J/(g-mole·°C) (25°C) (CRC 1980; CHRIS 1978)
Critical pressure	4,924 kPa (Kirk-Othmer 1978)
Critical temperature	289.45°C (Cheremisinoff 1979)
Coefficient of thermal expansion	$1.237 \times 10^{-3}/^{\circ}\text{C}$ (20°C) (Lange's Handbook 1979)
Thermal conductivity	0.139 W/(m·°C) (12°C) (Lange's Handbook 1979)
Saturation concentration	319 g/m ³ (20°C) (Verschuereen 1977) 485 g/m ³ (30°C) (Verschuereen 1977)
Diffusivity (vapour)	0.077 cm ² /s (0°C) (Perry 1973)
Evaporation rate	0.75 g/(m ² ·s) (20°C) (CHRIS 1974) 2.3 g/(m ² ·s) (20°C) (this work)
Octanol/water partition coefficient	2.14 (Cheremisinoff 1979)
Solubility	
In water	0.18 g/100 g (25°C) (Kirk-Othmer 1978)
In other common materials	Miscible in ethanol, diethyl ether, acetone, acetic acid and chloroform (CRC 1980) Miscible in carbon tetrachloride, carbon disulphide and toluene (Kirk-Othmer 1978)
Vapour Weight to Volume Conversion Factor	
	1 ppm = 3.242 mg/m ³ (20°C) (Verschuereen 1977)

BENZENE

CONVERSION NOMOGRAMS

**Pressure**

1 kPa = 1,000 Pa

**Viscosity****Dynamic** 1 Pa·s = 1,000 centipoise (cP)**Kinematic** 1 m²/s = 1,000,000 centistokes (cSt)**Concentration (in water)**1 ppm $\cong$ 1 mg/L**Energy (heat)**

1 kJ = 1,000 J

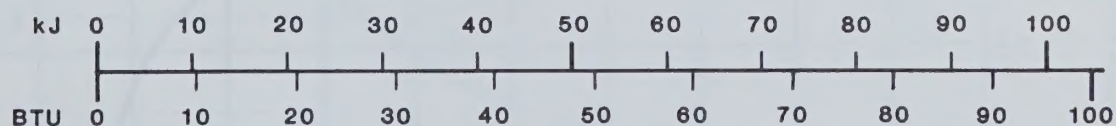
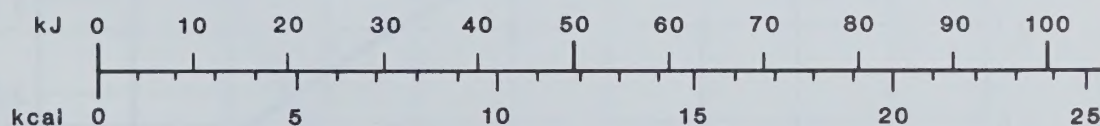
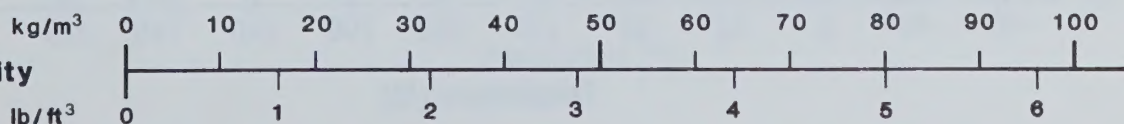
**Density**

FIGURE 1

BENZENE

VAPOUR PRESSURE
VS TEMPERATURE

Reference: Chem. Eng. 1975

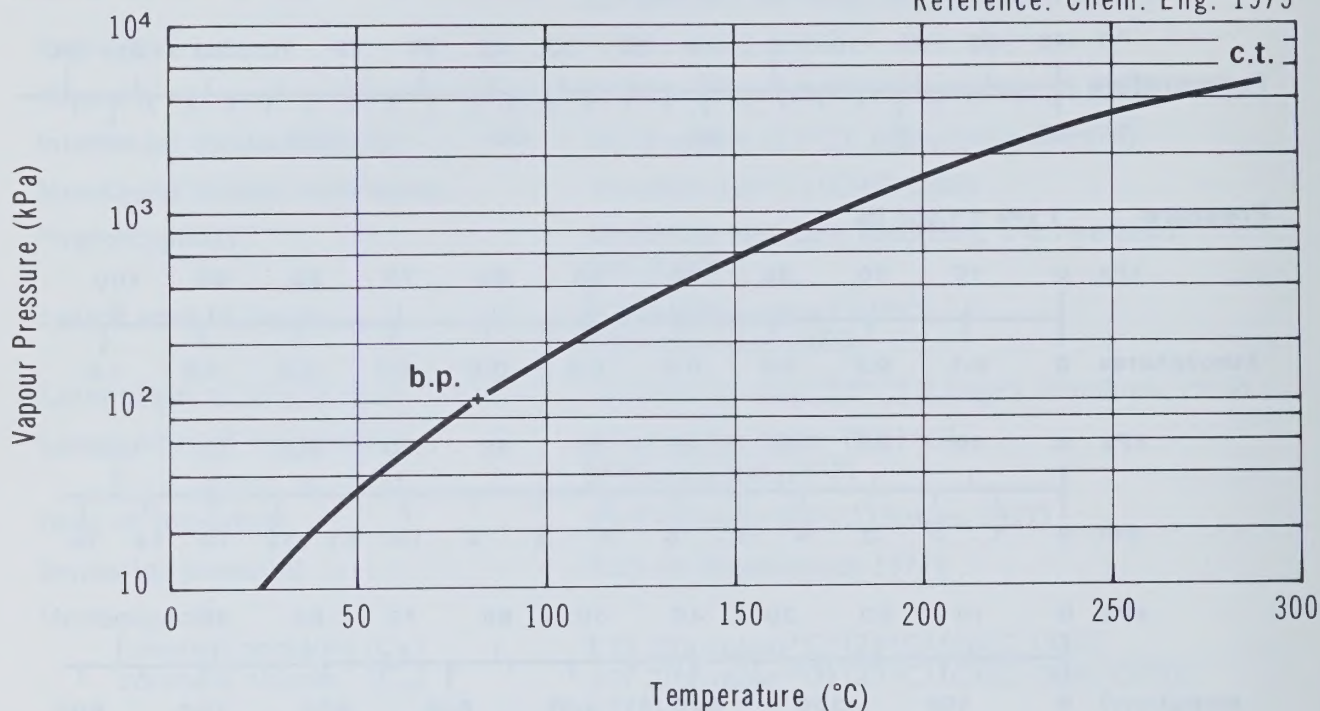
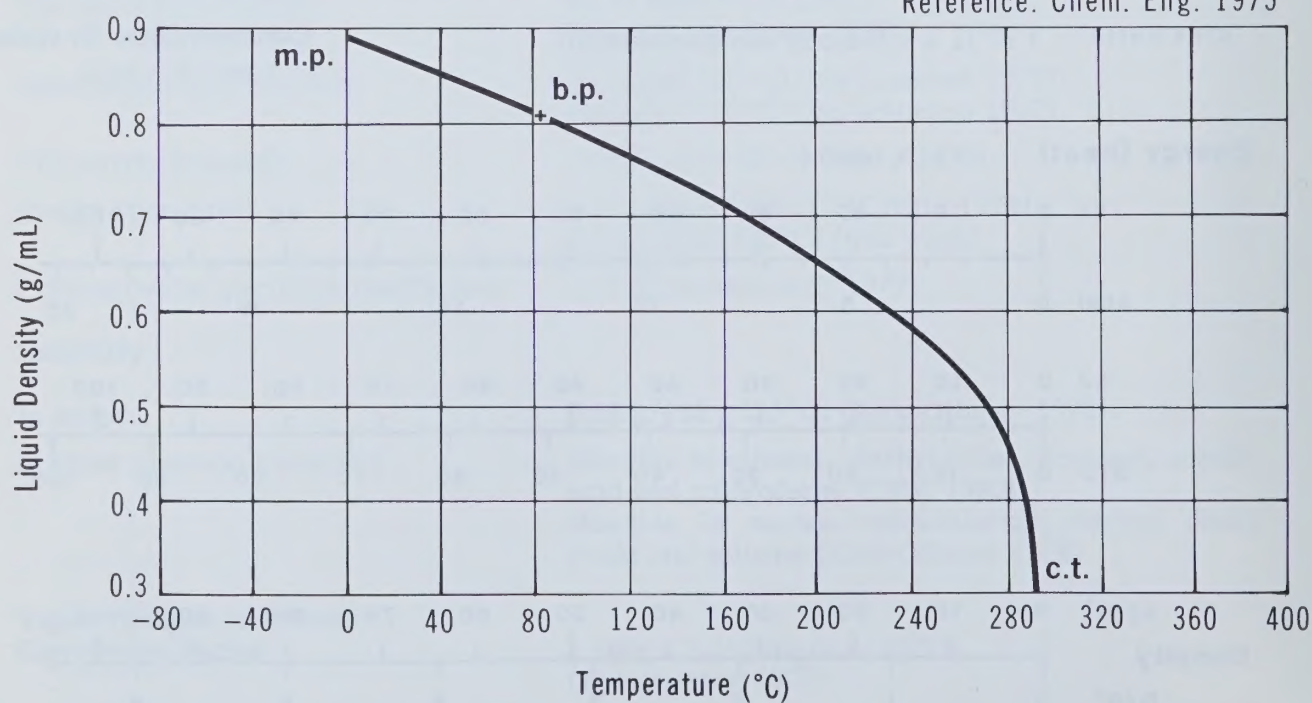


FIGURE 2

BENZENE

LIQUID DENSITY vs TEMPERATURE

Reference: Chem. Eng. 1975



BENZENE

SATURATED VAPOUR DENSITY vs TEMPERATURE

Reference: CHRIS 1978

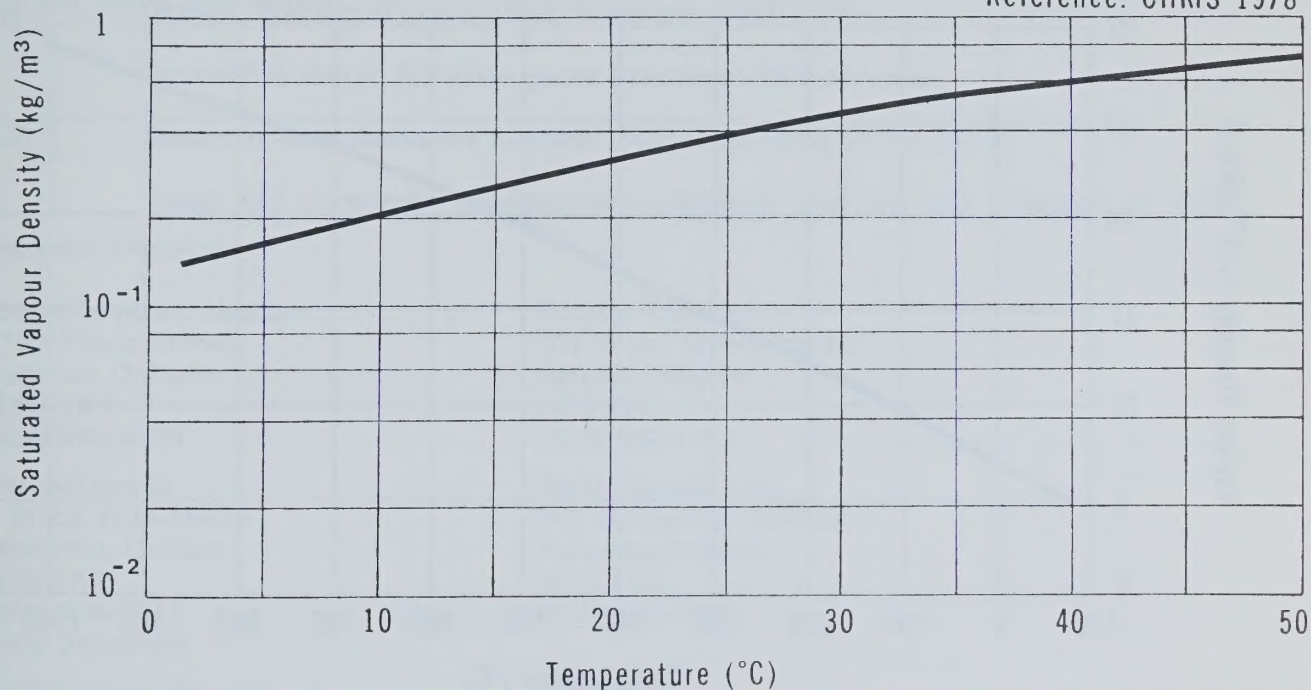


FIGURE 4

BENZENE

LIQUID VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1975

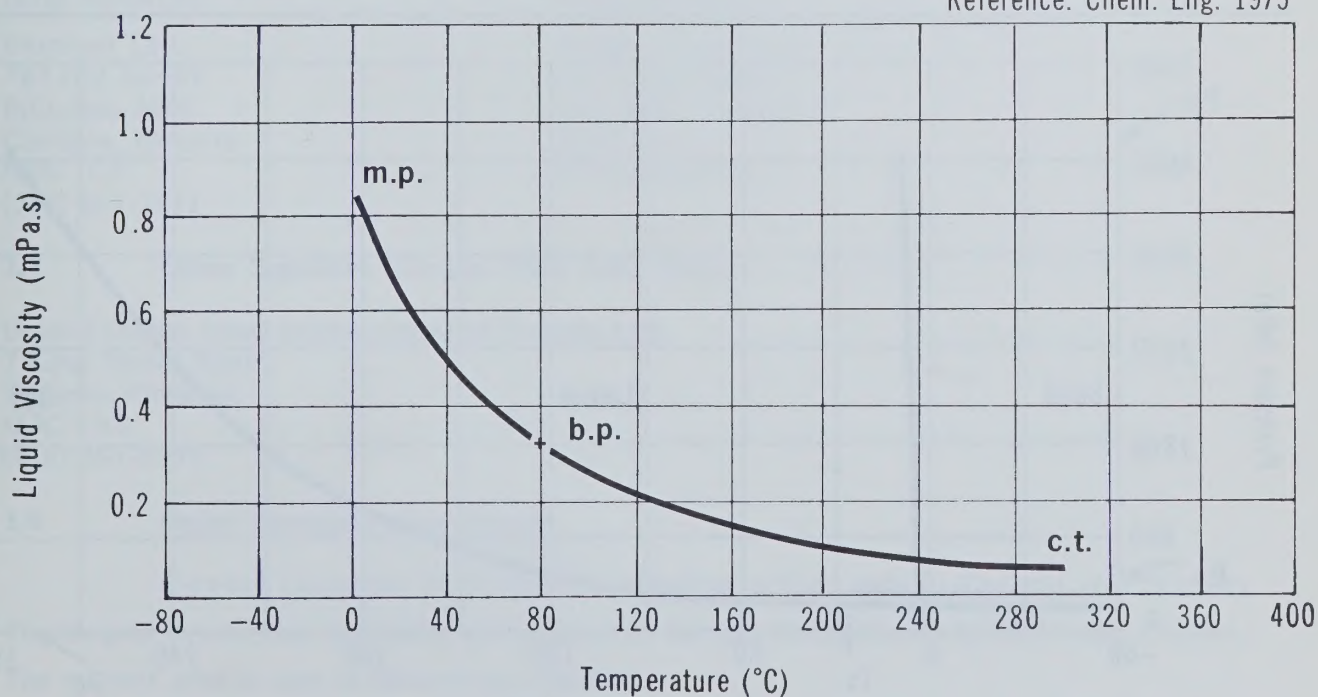


FIGURE 5

BENZENE

VAPOUR VISCOSITY vs TEMPERATURE

Reference: Chem: Eng. 1975

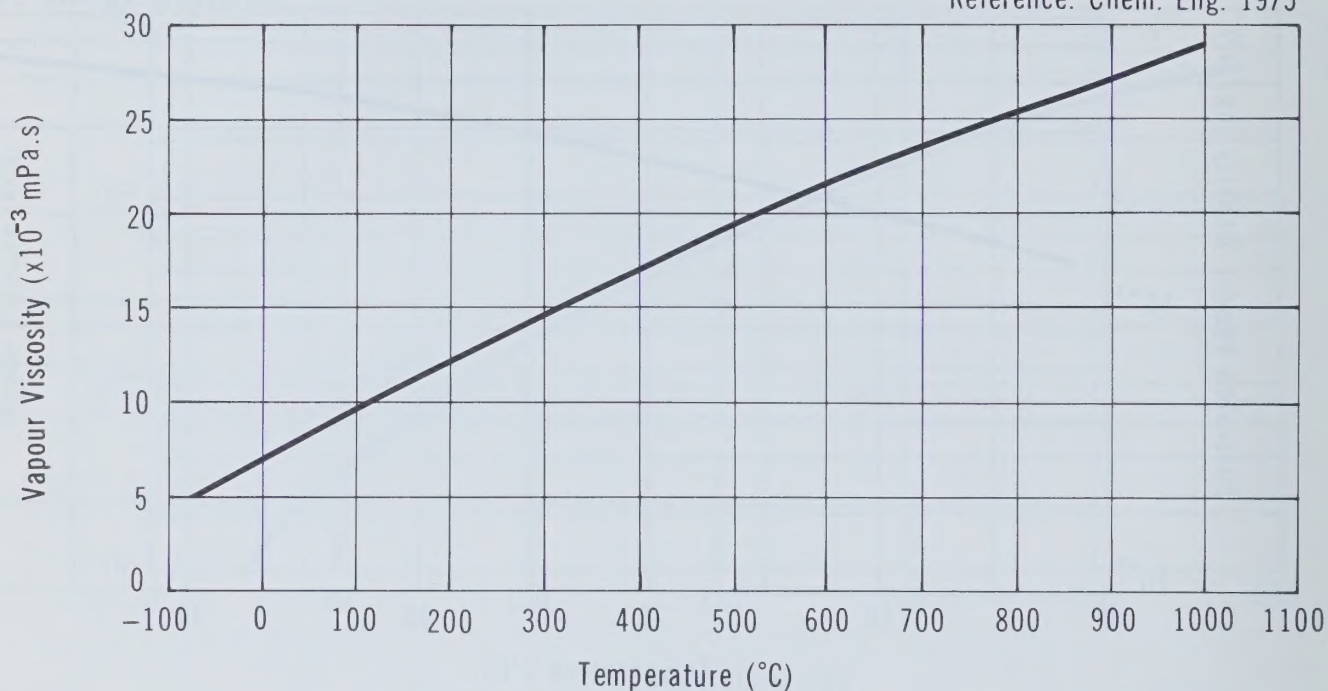
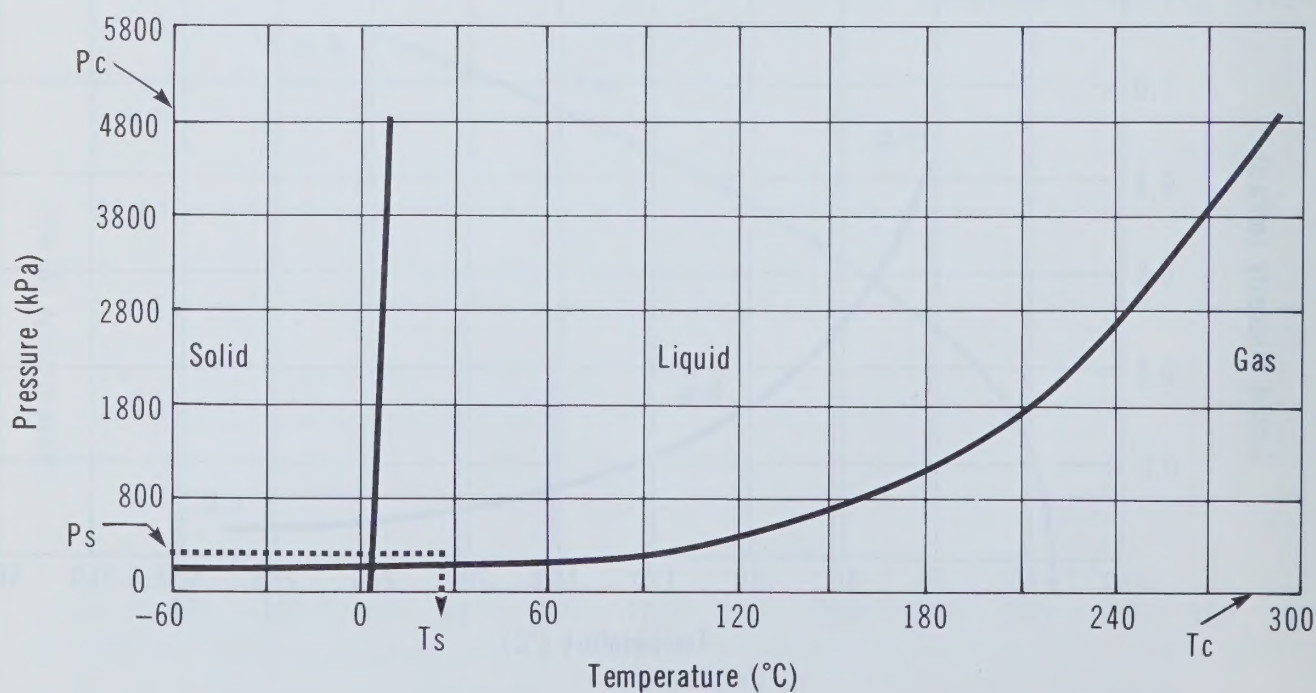


FIGURE 6

BENZENE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Corpus 1982; Finachem ASPI 1979)

Benzene is sold in nitration grade (minimum 99.0 percent).

3.2 Domestic Manufacturers (Corpus 1982; CBG 1980; CCPA 1981)

These are corporate headquarters addresses and are not intended as spill response contacts.

Esso Chemical Canada
2300 Yonge Street
Toronto, Ontario
M5W 1K3
(416) 488-6600

Polysar Limited
201 Front Street North
Sarnia, Ontario
N7T 7V1
(519) 332-1212

Petro-Canada
1 Place Ville-Marie
Montreal, Quebec
H3B 4A9
(514) 866-3911
(514) 866-2094

Shell Canada Ltd.
505 University Avenue
Toronto, Ontario
M5G 1X4
(416) 866-7111

Gulf Canada Products Co.
Div. of Gulf Canada Ltd.
800 Bay Street
Toronto, Ontario
M5S 1Y8
(416) 924-4141

Sunchem
Division of Sunoco Inc.
56 Wellesley Street West
Toronto, Ontario
M5S 2S4
(416) 924-4111

Petrosar Ltd.
785 Hill Street
P.O. Box 7000
Corunna, Ontario
N0N 1G0
(519) 862-2911

Texaco Canada Inc.
90 Wynford Drive
Don Mills, Ontario
M3C 1K4
(416) 443-7811

3.3 Other Suppliers (Corpus 1982; CBG 1980)

United States Steel International of Canada Ltd.
7 King Street East
Toronto, Ontario
M5C 1A8
(416) 364-6291

3.4 Major Transportation Routes

Current Canadian production of benzene occurs only in Ontario and Quebec. The largest production facilities are located in Sarnia, Ontario, and in Montreal, Quebec. The market area is also in Ontario and Quebec.

3.5 Production Levels (Corpus 1982; CCP 1981; Finachem PDS 1981)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1981)
Esso Chemical Canada, Sarnia, Ont.	100
Petro-Canada, Montreal, Que.	145
Gulf Canada, Montreal, Que.	119
Petrosar, Corunna, Ont.	165
Polysar, Sarnia, Ont.	67
Shell Canada, Corunna, Ont.	67
Sunchem, Sarnia, Ont.	63
Texaco Canada, Mississauga, Ont.	20
TOTAL	746
Domestic Production (1980)	566.5
Imports (1980)	3
TOTAL	569.5

3.6 Future Development (CCP 1980, 1981; Corpus 1982)

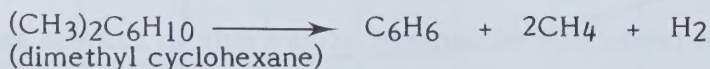
Texaco, in the future, will switch its benzene production from Mississauga to Nanticoke, Ontario, where its operations are more modern.

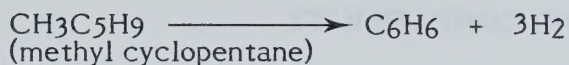
Two benzene extraction/dealkylation facilities are being planned for refineries in Alberta and are to come on-stream prior to 1985. These are: Shell/Husky in Scotford (235 kt/yr) and Gulf Canada in Edmonton (98 kt/yr (1983); 224 kt/yr (1985)). Gulf Canada's Montreal East refinery will have increased its output by 46 kt/yr by 1983. Thus, the total projected capacity of these three companies is 624 kt/yr.

3.7 Manufacture of Benzene

3.7.1 General. Benzene is produced in Canada mainly from petroleum feedstock reformation and hydrodealkylation of substituted aromatics.

3.7.2 Manufacturing Process. Petroleum naphtha from the cracking and fractionating of crude oil is partially converted to benzene and other aromatics by exposing it to a platinum catalyst at elevated temperatures. Some possible reactions are:





Overall benzene content may be 5 to 10 percent. This is recovered and purified using processes such as fractional distillation and solvent extraction.

Benzene and methane may be produced by the catalyzed reaction of toluene and hydrogen:



Benzene is recovered by fractional distillation.

3.8 Major Uses in Canada (Corpus 1981; Finachem ASPI 1979)

Benzene is used in the production of ethylbenzene/styrene, cumene, cyclohexane and maleic anhydride.

3.9 Major Buyers in Canada (Corpus 1982; CBG 1980)

Dow Chemical Canada, Inc., Sarnia, Ont.
 Petro-Canada, Montreal, Que.
 Gulf Canada Products Company, Montreal East, Que.
 Monsanto Canada Inc., LaSalle, Que.
 Polysar Ltd., Sarnia, Ont.*
 Recochem Inc., Montreal, Que.

* Single largest buyer, with Dow Chemical being second (CCP 1981).

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Transportation vessels and containers under this category have been grouped under the classifications of railway tank cars, highway tank vehicles and portable tanks. Significant production volumes are also transferred by pipeline in Canada.

4.1.1.1 Railway tank cars. Railway tank cars used to transport benzene are described in Table 2 (TCM 1979). Benzene is usually shipped in railway tank cars with capacities of 64,400 L (14,000 Imp. gal.), 75,700 L (16,700 Imp. gal.), 90,900 L (20,000 Imp. gal.), and 114,000 L (25,000 Imp. gal.). Figure 7 shows a class 111A60W1 railway car used to transport benzene; Table 3 indicates railway tank car details associated with this drawing. Cars are equipped for unloading by pump or gravity flow through bottom outlets provided with inner plug valves (TDGC 1980). Benzene is usually unloaded from top fittings, with pumps or under nitrogen pressure. In this case, the benzene is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with an unloading connection valve. Air pressure is never used for unloading benzene tanks (MCA 1960).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

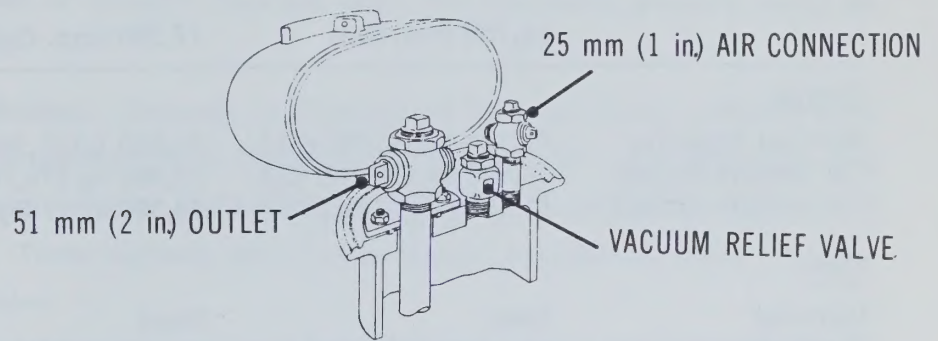
CTC/DOT* Specification Number	Description
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A60F1	Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A100W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Bottom outlet or washout optional. Test pressure 690 kPa (100 psi).

* Canadian Transport Commission and Department of Transportation (U.S.)

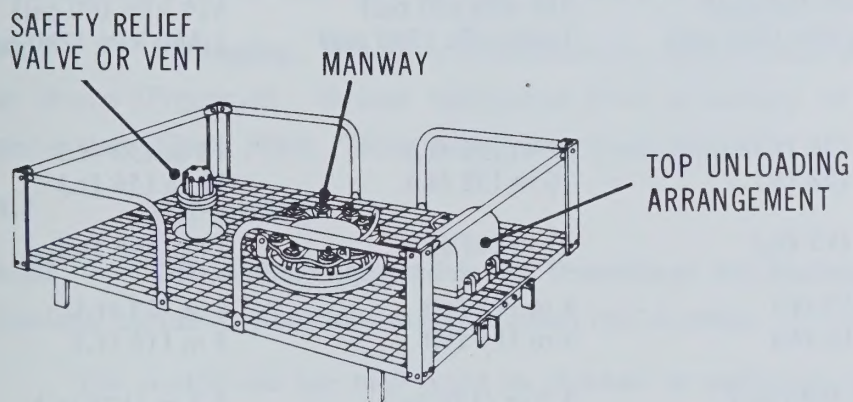
BENZENE

RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979; RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

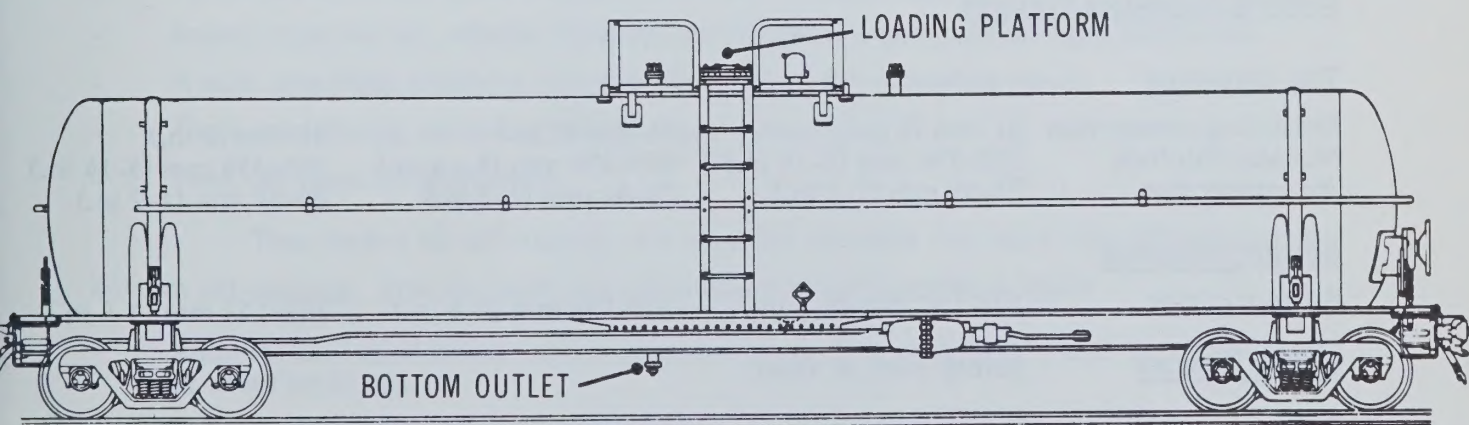


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A60W1
(TCM 1979; RTDCR 1974)

Description	Tank Car Size		
	16,700 Imp. Gal.	17,200 Imp. Gal.	20,000 Imp. Gal.
<u>Overall</u>			
Nominal capacity	75,700 L (16,700 gal.)	78,000 L (17,200 gal.)	90,900 L (20,000 gal.)
Car weight- empty	33,900 kg (74,700 lb.)	33,900 kg (74,700 lb.)	38,900 kg (85,800 lb.)
Car weight- (max.)	119,000 kg (262,000 lb.)	83,500 kg (184,000 lb.)	119,000 kg (262,000 lb.)
<u>Tank</u>			
Material	Steel	Steel	Steel
Thickness	11.1 mm (7/16 in.)	11.1 mm (7/16 in.)	11.1 mm (7/16 in.)
Inside diameter	2.60 m (102 in.)	2.62 m (103 in.)	2.74 (108 in.)
Test pressure	414 kPa (60 psi)	414 kPa (60 psi)	414 kPa (60 psi)
Burst pressure	1,640 kPa (240 psi)	1,640 kPa (240 psi)	1,640 kPa (240 psi)
<u>Approximate Dimensions</u>			
Coupled length	17 m (56 ft.)	17 m (56 ft.)	18 m (59 ft.)
Length over strikers	16 m (52 ft.)	16 m (52 ft.)	17 m (56 ft.)
Length of truck centers	13 m (43 ft.)	13 m (43 ft.)	14 m (46 ft.)
Height to top of grating	4 m (13 ft.)	4 m (13 ft.)	4 m (13 ft.)
Overall height	5 m (16 ft.)	5 m (16 ft.)	5 m (16 ft.)
Overall width (over grabs)	3.2 m (126 in.)	3.2 m (126 in.)	3.2 m (126 in.)
Length of grating	2-3 m (7-10 ft.)	2-3 m (7-10 ft.)	2-3 m (7-10 ft.)
Width of grating	1.5-2 m (5-7 ft.)	1.5-2 m (5-7 ft.)	1.5-2 m (5-7 ft.)
<u>Loading/Unloading Fixtures</u>			
<u>Top Unloading</u>			
Unloading connection	51 mm (2 in.)	51 mm (2 in.)	51 mm (2 in.)
Manway/fill hole	203-356 mm (8-14 in.)	203-356 mm (8-14 in.)	203-356 mm (8-14 in.)
Air connection	25-51 mm (1-2 in.)	25-51 mm (1-2 in.)	25-51 mm (1-2 in.)
<u>Bottom unloading</u>			
Bottom outlet	102-152 mm (4-6 in.)	102-152 mm (4-6 in.)	102-152 mm (4-6 in.)
<u>Safety Devices</u>	Safety vent or valve		
<u>Dome</u>	None		
<u>Insulation</u>	Optional		

A safety relief valve set at 241 kPa (35 psi) for 111A60W1 cars and 517 kPa (75 psi) for 111A100W1 cars is required (TCM 1979). A gauging device, either the rod type or the tape type, is optional. The top unloading connection must be protected by a housing. The maximum pressure allowable for the CTC/DOT 111A100W1 rail cars is 448 kPa (65 psi). When the 111A60W1 or 111A60F1 cars are used, this maximum pressure would be 276 kPa (40 psi) (TCM 1979).

4.1.1.2 Tank motor vehicles. Benzene is transported by tank motor vehicles with tanks classed as nonpressure vessels (TDGC 1980). Design pressure for such tanks does not exceed 14 kPa (2 psi). Motor vehicle tanks carrying benzene are similar to the railway tanks previously described. These highway tankers are usually unloaded by pump from the top unloading connection valve.

The off-loading equipment and procedures for tank motor vehicles are similar to those for railway tank cars (see Section 4.2.1).

4.1.2 Packaging. Benzene, in addition to railway bulk shipments, is also transported in drums (Figure 8). Drums fabricated from a variety of construction materials are permitted (TDGC 1980). Table 4 describes these drums.

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (MCA 1960):

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution signs displayed.
- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- Tank car must be grounded.

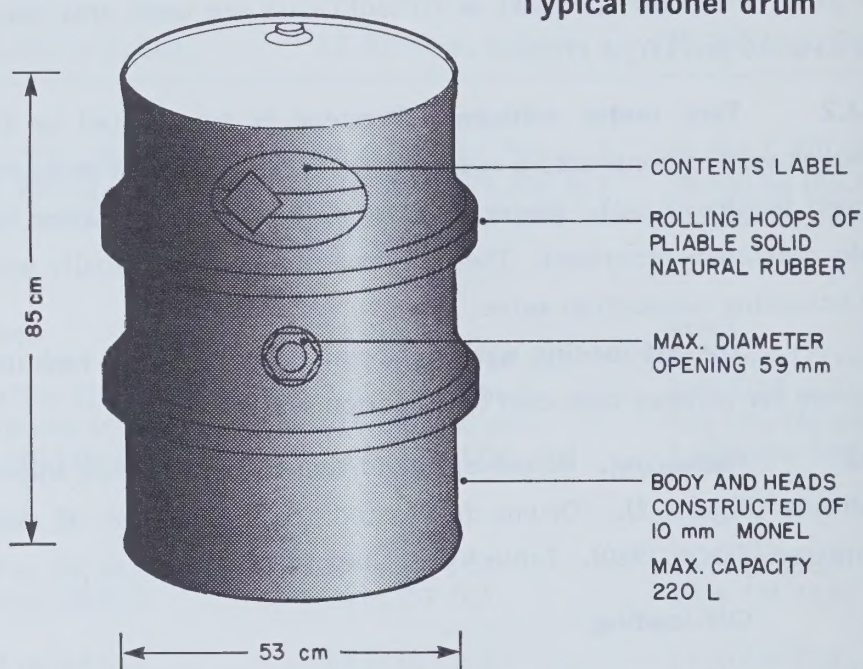
Two means of off-loading are used for benzene rail cars, top off-loading and bottom off-loading. Proceed with top off-loading as follows (MCA 1960):

- Relieve tank of internal vapour pressure by cooling tank with water or venting tank at short intervals.

BENZENE

TYPICAL DRUM CONTAINERS

Typical monel drum



Typical steel drum

MIN. 2.4 mm
LEAD COATING FOR
IAC DESIGNATION

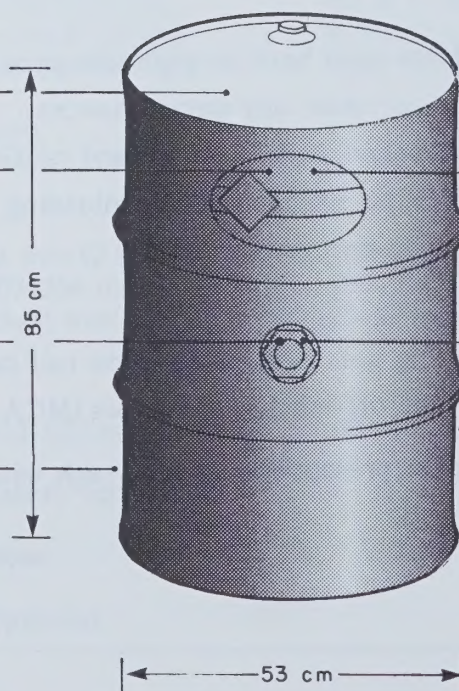
CONTENTS LABEL

MAX. DIAMETER
OPENING 70 mm

BODY AND HEADS
CONSTRUCTED OF
ROLLED STEEL

MAX. CAPACITY
250 L

MAX. NET MASS
400 kg



Typical aluminum drum

CONTENTS LABEL

MAX. DIAMETER
OPENING 70 mm

BODY AND HEADS
CONSTRUCTED OF
MIN. 99% PURE
ALUMINUM

MAX. CAPACITY
250 L

MAX. NET MASS
400 kg

TABLE 4 DRUMS

Type of Drum	Designation	Description	Figure No. (If Any)
Steel	1A1	Nonremovable head, reusable	8
	1A1A	1A1 with reinforced chime	8
	1A1B	1A1 with welded closure flange	8
	1A1D	1A1 with coating (other than lead)	8
	1A2	Removable head, reusable	8
	1A3	Nonremovable head, single use only	8
Monel*	TC5M	Nonremovable head	8
Aluminum	1B1	Nonremovable head	8
	1B2	Removable head	8
Steel with inner plastic receptacles	6HA1	Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity of 225 L (49 Imp. gal.)	
Fibreboard with inner plastic receptacles	6HG1	Outer container of convolutely wound plies of fibreboard. Inner plastic receptacle in shape of drum. Maximum capacity of 225 L (49 Imp. gal.)	

* See Section 4.3 of this report.

- After removing the protective housing from the discharge line at the top of the car, connect the 51 mm (2 in.) unloading line.
- Off-load the tanker by pump or with the application of a controlled nitrogen pad.

Proceed with bottom off-loading in the following manner using gravity flow or pump:

- Relieve internal pressure as previously mentioned.
- After connecting the unloading line to a bottom outlet, open the inside bottom valve by turning the valve rod handle at the top or bottom of the car.
- Off-load the car by gravity or pump.

4.2.2 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in benzene service. It is recognized that other materials may be used for particular applications. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets, and pumps.

Schedule 40 seamless ASTM A106 carbon steel pipes and fittings lined with chlorinated polyether resins are recommended for benzene lines (DCRG 1978). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak after a very short time. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipeline should be tested with air at pressures from 345 to 518 kPa (50 to 75 psi) and all leaks carefully stopped. If leaks develop in service, the only satisfactory way to repair them is to chip out the bad weld and reweld, or replace the section of pipe.

The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on benzene tank cars; however, process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining.

Flexible bellows-type expansion joints should be used for the flexible sections of the unloading line. They are manufactured with ASA ductile iron flanges with expansion members molded from tetrafluoroethylene resin (Dow PPS 1972). Some installations of flexible line are made with standard lined fittings using a number of flanged elbows.

For valving, cast iron or cast steel diaphragm valves lined with chlorinated polyether or polyvinylidene chloride resin will serve adequately (Dow PPS 1972). Viton, asbestos or Teflon may be used as a gasket material at normal temperature ranges (DCRG 1978).

A single-suction sealless magnetic drive centrifugal pump with "wet end" material of 316 stainless steel gives good results (ASS). Leakage from this type of pump is virtually eliminated. Provision must be made for draining the pump so that repairs can be made safely. The pump should be equipped with flanges at both suction and discharge openings; screw connections are more subject to leakage and should be avoided.

4.3 Compatibility with Materials of Construction

The compatibility of benzene with materials of construction is shown in Table 5. The unbracketed abbreviations are described in Table 6. The rating system for this report is briefly described below.

<u>Recommended:</u>	This material will perform satisfactorily in the given application.
<u>Conditional:</u>	Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.
<u>Not Recommended:</u>	Material will be severely affected in this application and should not be used.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings					PE ABS PVC I PVC II (DPPED 1967) Plastics Rubber (CCPA 1982)
		79	PP (DCRG 1978)		
	100%	21	CS (MCA 1960)		
		66	Chlorinated Polyether (DCRG 1978)		
		52	PVDF (DCRG 1978)		
		24	PVDC (DCRG 1978)		
2. Valves	(Coal Tar or Crude Oil)	21	SS 316 (JSSV 1979)		
	(Crude Oil)	Boiling	SS 316 (JSSV 1979)		

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
2. Valves (cont'd)	(Coal Tar or Crude Oil)	Hot	SS 316 (JSSV 1979)		
3. Pumps	100%	38	GRP with FPM "O" Ring		
4. Storage	100%	21	CS (MCA 1960)		
5. Others		21	PVDF (TPS 1978)		
		22			PVC CPVC (TPS 1978)
		23		PP (TPS 1978)	
		49			PP (TPS 1978)
		66			PVDF (TPS 1978)
		20	SS 302 SS 304 SS 316 (ASS)		
	(Coal Tar or Crude Oil)	Boiling	SS 302 SS 304 SS 316 (ASS)		
	Technically Pure	20	POM FPM (GF)	NBR (GF)	uPVC PE PP NR IIR EPDM CR CSM (GF)
	100%				NR SBR CR NBR IIR

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (cont'd)	100%				CSM Si EPDM (GPP)
	To 70%	24 - 100	Glass (CDS 1967)		
	100%	24 - 100	Glass (CDS 1967)		
	100%	24			Concrete (CDS 1967)
	100%	24	Wood (CDS 1967)		

TABLE 6 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile/Butadiene Styrene
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
	Chlorinated Polyether
CSM	Chlorosulphonated Polyethylene (Hypalon)
CPVC	Chlorinated Polyvinyl Chloride
	Concrete
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
GRP	Glass Reinforced Vinyl Ester
IIR	Isobutylene/Isoprene (Butyl)
NBR	Acrylonitrile/Butadiene Rubber (Nitrile, Buna N)
NR	Natural Rubber
	Nickel-Copper Alloy (Monel)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (Followed by grade, if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
Si	Silicone
SBR	Styrene/Butadiene Rubber (GR-5, Buna S)
SS (Followed by grade)	Stainless Steel
uPVC	Unplasticized Polyvinyl Chloride
	Wood

5 CONTAMINANT TRANSPORT

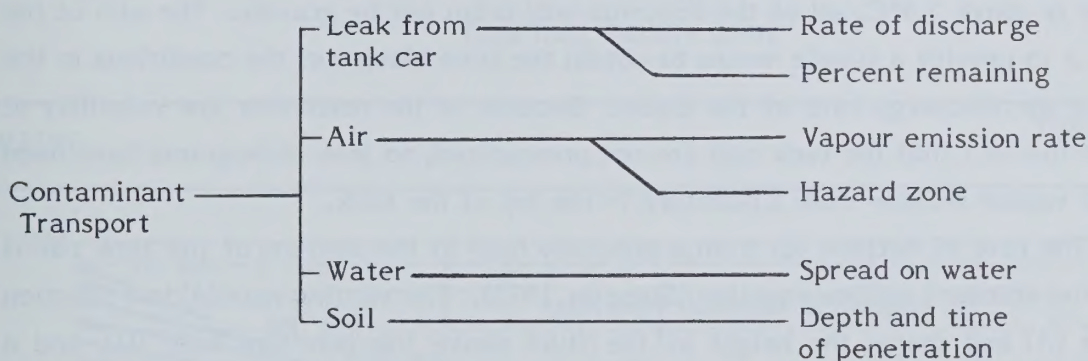
5.1 General Summary

Benzene is a colourless, volatile liquid that is commonly transported in railway tank cars. When spilled in the environment, it will form a liquid pool, spreading on the surface of a water body or on the ground, being adsorbed onto the soil. The vapour is released continuously to the atmosphere by evaporation.

When spilled on water, the slick has a natural tendency to spread. Since it is only slightly soluble and is less dense than water, only a very small amount will be dissolved in the water, the rest evaporating to the atmosphere until it is removed.

Benzene when spilled on the ground is gradually adsorbed onto the soil, at a rate dependent on the soil type and its degree of saturation with water. At the same time, the downward transport of the liquid toward the groundwater table may cause environmental concerns.

The following factors are considered for the transport of a benzene spill in the air, water and soil media:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Benzene is commonly transported in railway tank cars as a non-pressurized liquid. While the capacities of the tank cars vary widely, one tank car size

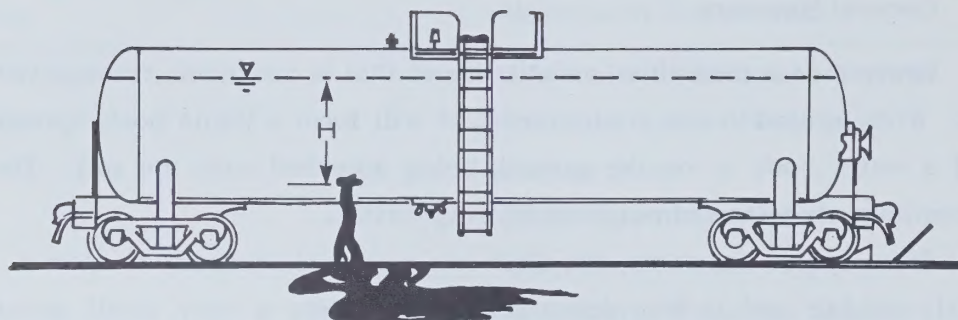


FIGURE 9 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80,000 L.

If a tank car loaded with benzene is punctured on the bottom and the liquid temperature is above 5.5°C, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the discharge rate of the liquid. Because of the relatively low volatility of benzene and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

The rate of outflow (q) from a puncture hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). The venting rate (q) is a function of hole size (A) and shape, the height of the fluid above the puncture hole (H), and a coefficient of discharge (C_d). For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

5.2.2 Nomograms.

5.2.2.1 Figure 10: Percent remaining versus time. Figure 10 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car (2.75 m $\varnothing$ x 13.4 m long) is assumed to be initially full (at $t=0$) with a volume of about 80,000 L of benzene. The amount remaining at any time

FIGURE 10

BENZENE

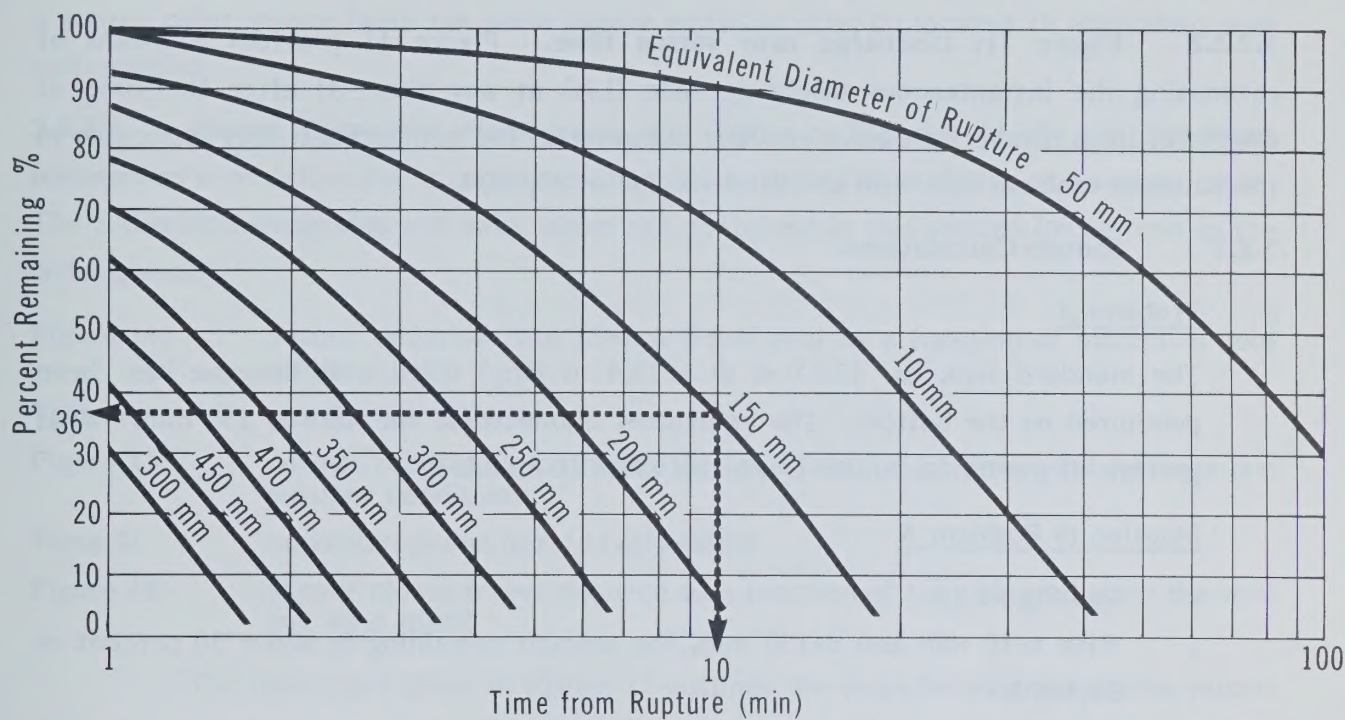
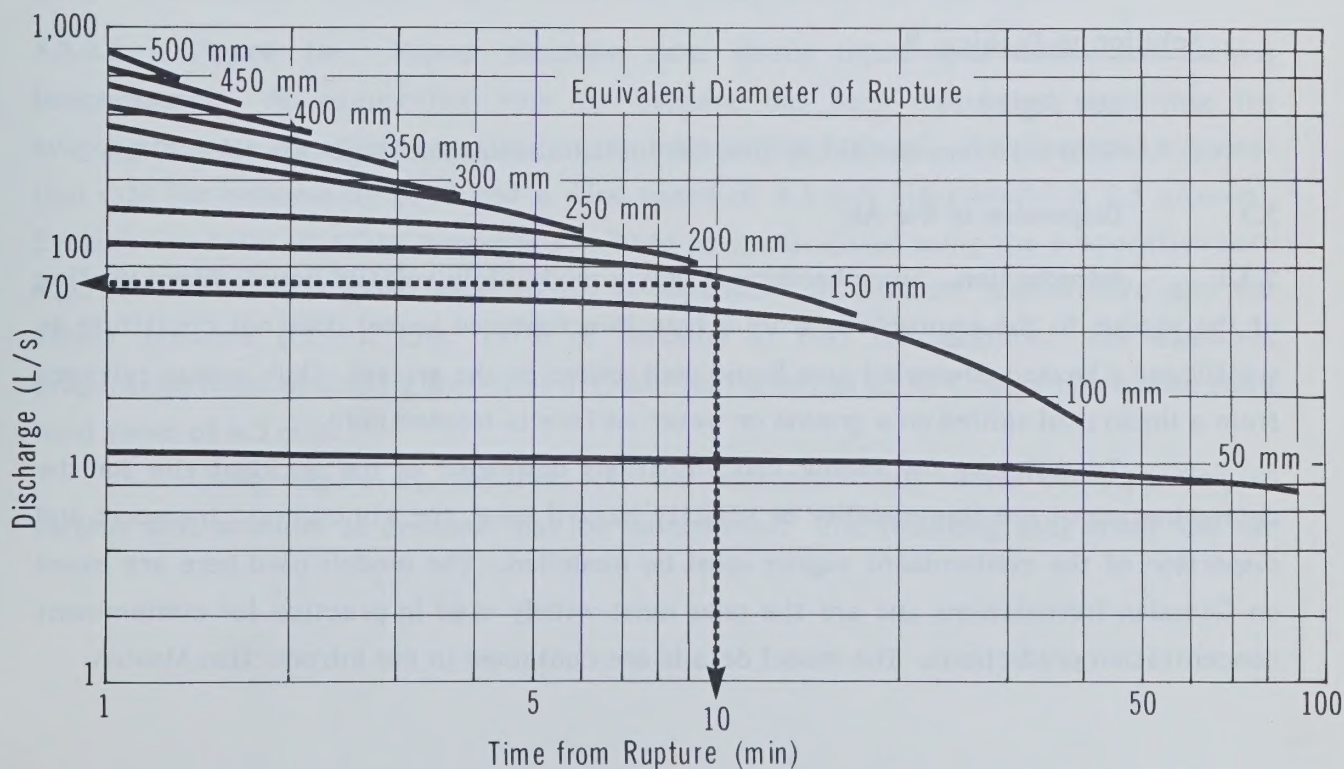
PERCENT REMAINING
VS TIME

FIGURE 11

BENZENE

DISCHARGE RATE
VS TIME

(t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

5.2.2.2 Figure 11: Discharge rate versus time. Figure 11 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture, for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80,000 L.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car (2.75 m $\varnothing$ x 13.4 m long) filled with benzene has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80,000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 10
- With $t=10$ min and $d=150$ mm, the amount remaining is about 36 percent or 28,800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- Use Figure 11
- With $t=10$ min and $d=150$ mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since benzene is only a moderately volatile liquid, direct venting of the vapour to the atmosphere from a hole in a ruptured vessel does not constitute as significant a hazard downwind as a liquid pool spilled on the ground. Only vapour released from a liquid pool spilled on a ground or water surface is treated here.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 12 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source as a virtual point source (with the same vapour emission rate, Q) located 10 equivalent pool radii upwind.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in the order given):

- Figure 14: vapour emission rate from a liquid pool as a function of maximum pool radius
- Table 7: weather conditions
- Figure 15: normalized vapour concentration as a function of downwind distance and weather conditions
- Table 8: maximum plume hazard half-widths
- Figure 18: vapour plume travel distance as a function of time elapsed since the spill and wind speed

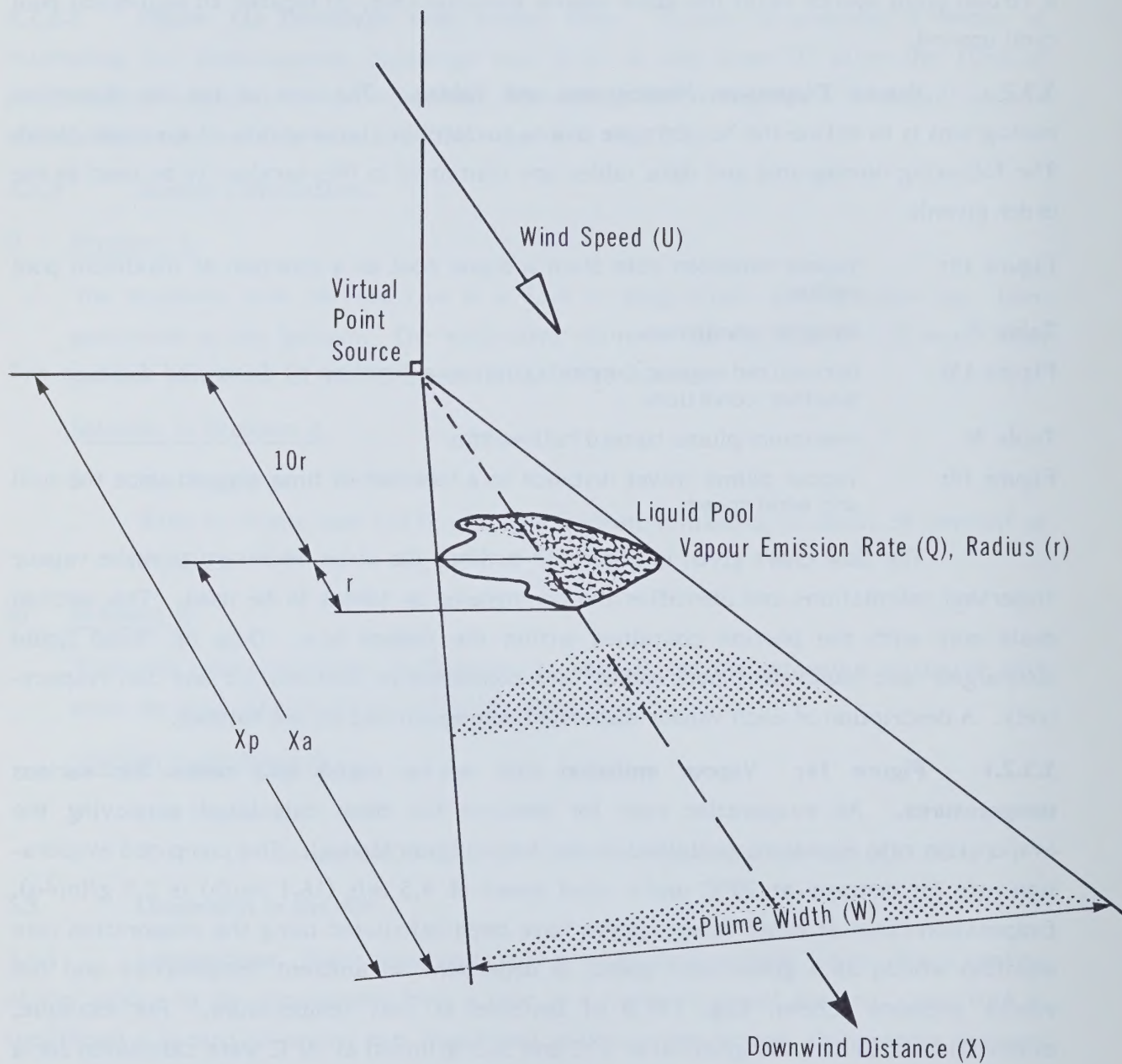
The flow chart given in Figure 13 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" and "equivalent pool radius" are contained in Sections 5.2 and 5.4, respectively. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 14: Vapour emission rate versus liquid spill radius for various temperatures. An evaporation rate for benzene has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for benzene at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 2.3 g/(m²·s). Evaporation rates at other temperatures have been calculated using the evaporation rate equation which, at a given wind speed, is dependent on ambient temperature and the vapour pressure (Chem. Eng. 1975) of benzene at that temperature. For example, evaporation rates of 0.051 g/(m²·s) at 0°C and 3.25 g/(m²·s) at 30°C were calculated for a wind speed of 4.5 m/s.

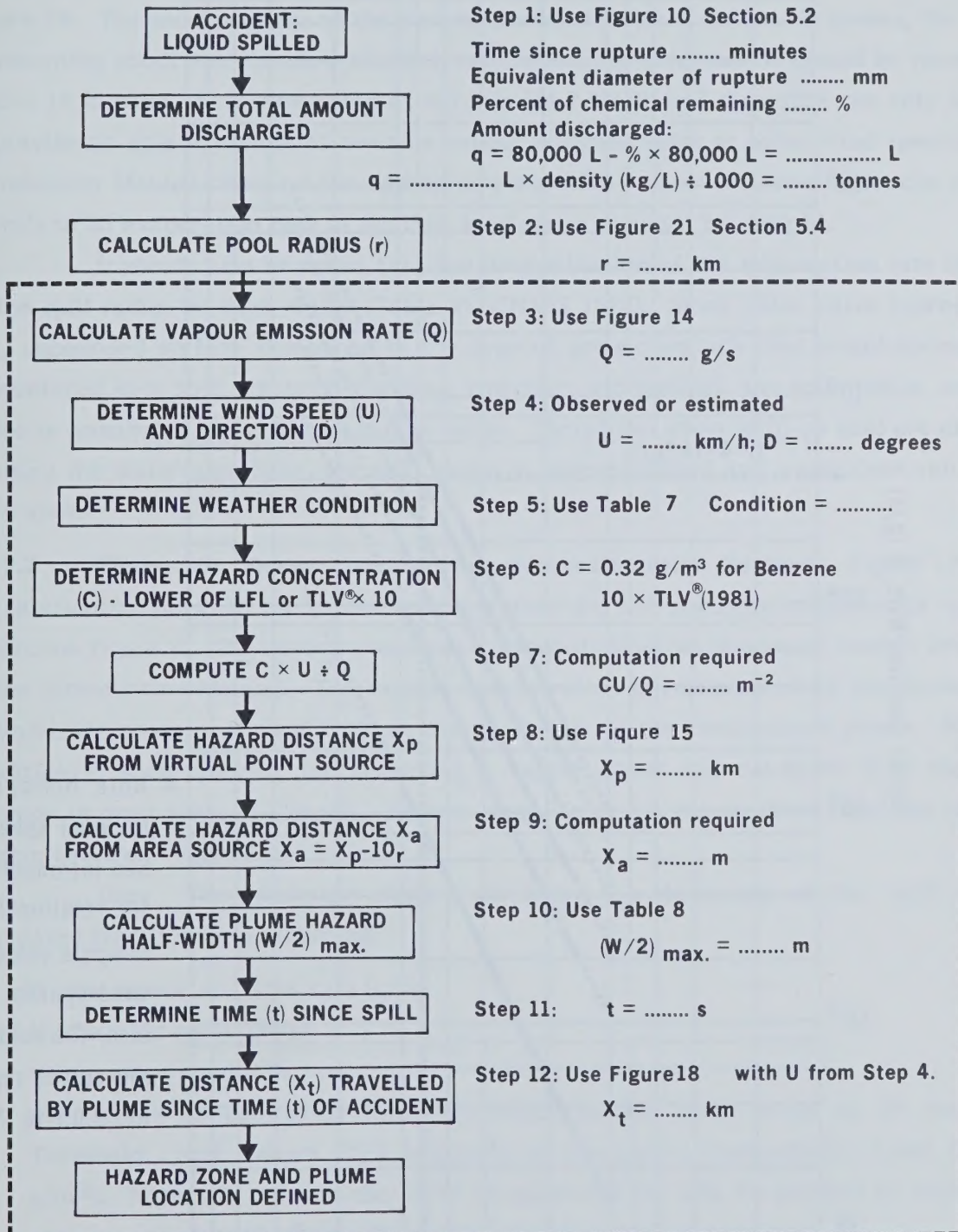
Using Figure 21, Section 5.4, the maximum spill radius corresponding to various spill amounts of benzene may be determined. The resulting spill areas and the

BENZENE

SCHEMATIC OF CONTAMINANT PLUME

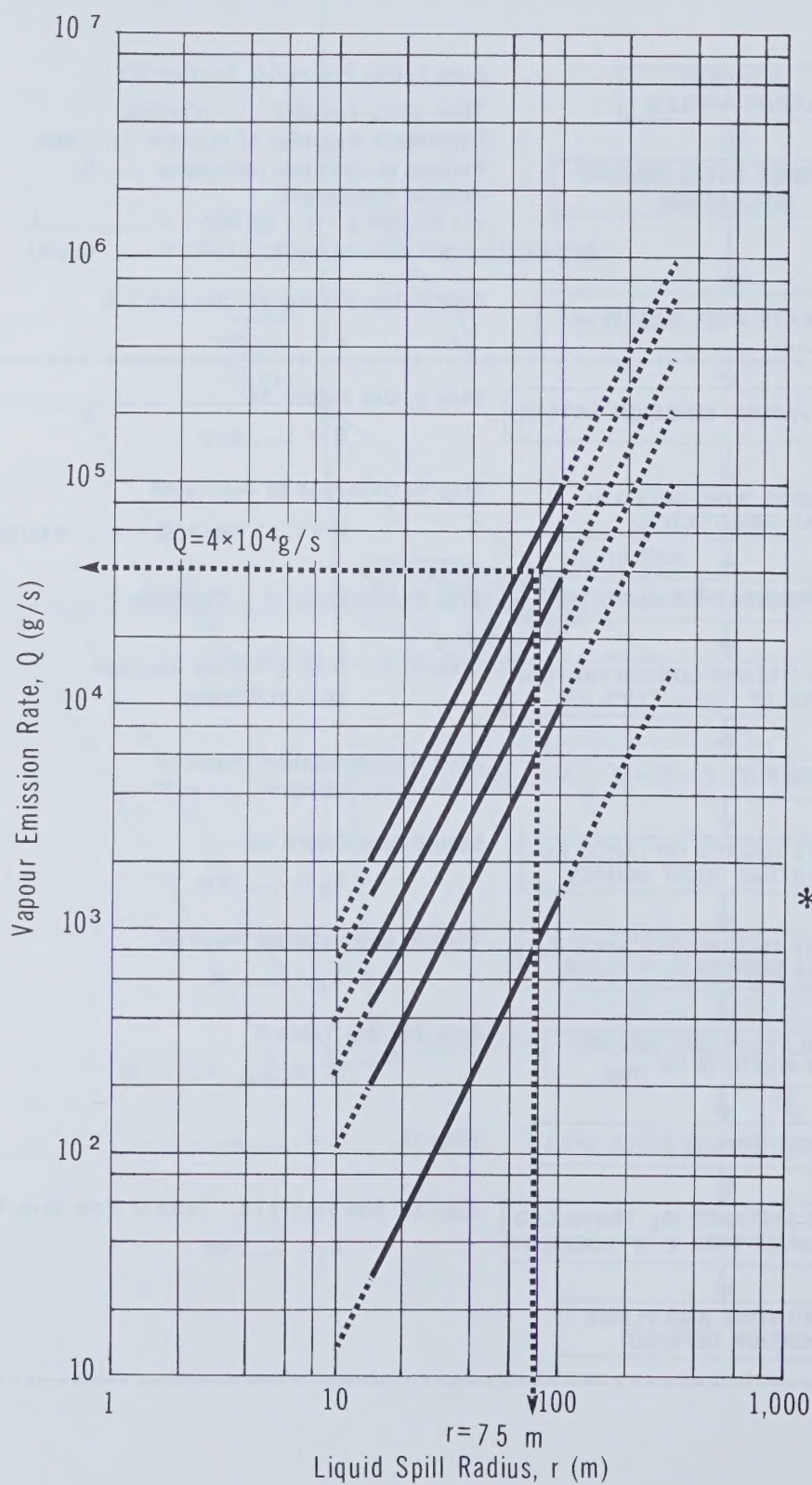


BENZENE

FLOW CHART TO DETERMINE
VAPOUR HAZARD ZONE

BENZENE

VAPOUR EMISSION RATE VS LIQUID SPILL RADIUS FOR VARIOUS TEMPERATURES *



* Note: Nomogram applies for wind speed of 4.5 m/s. See Introduction Manual for relationship to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.05 to 70 tonnes

benzene evaporation rates provide the basis for preparation of the vapour release rate versus spill radius nomogram (Figure 14).

Use: For a pool of benzene of known radius, the rate (Q) at which benzene vapour is released to the atmosphere at a given temperature can then be estimated from Figure 14. The solid portions of the curves represent spills of 0.05 to 70 tonnes, the latter representing about one standard 80,000 L rail car load of benzene. It should be noted that Figure 14 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of benzene vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

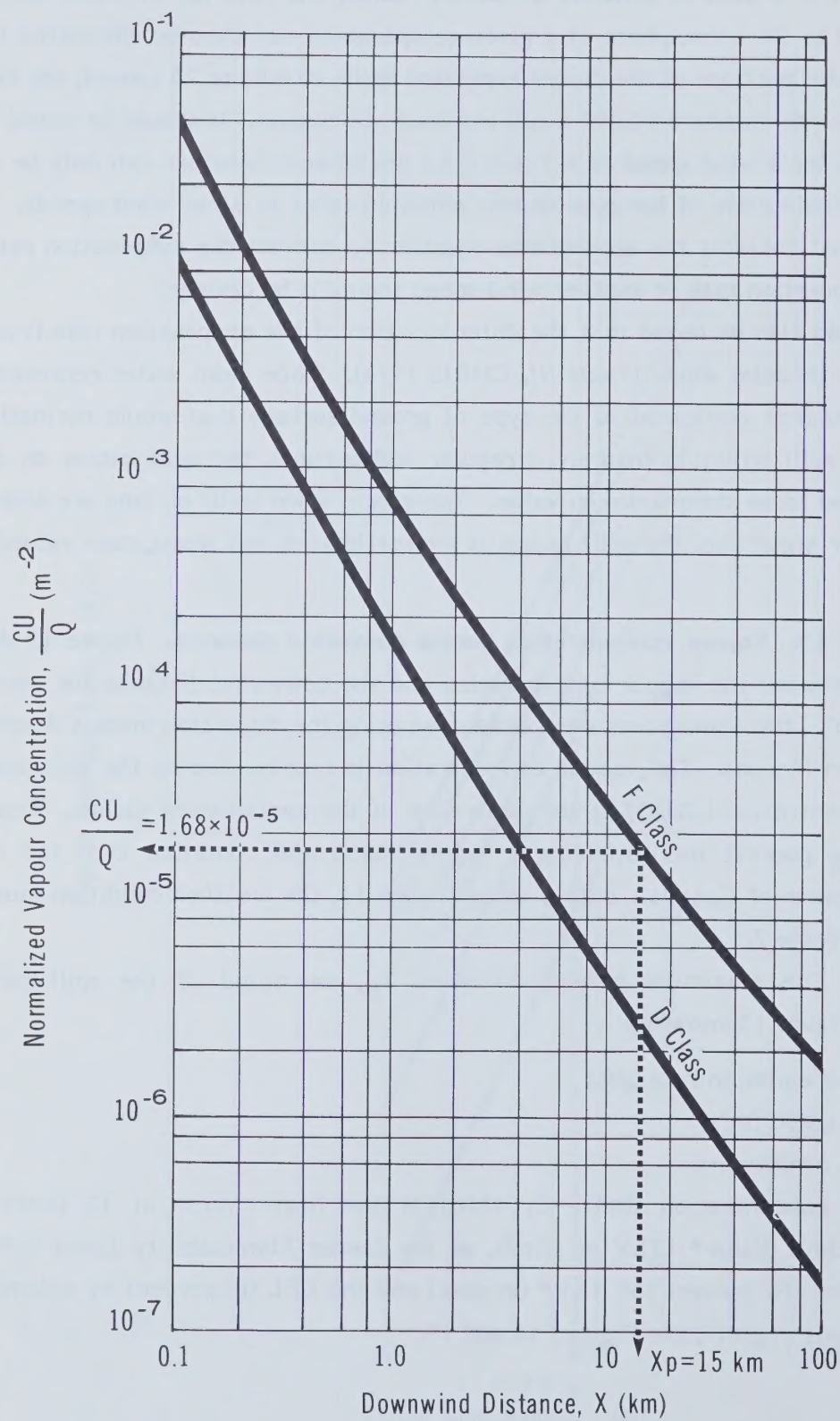
It should also be noted that the determination of the evaporation rate is based on the spill radius on calm water (Table VI, CHRIS 1974). Since calm water represents a flat, unbounded surface compared to the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous), the spill radius on calm water is considered to be the maximum value. Therefore, when spills on land are assessed by using the water algorithm, the spill radius is overestimated and worst case values are generated.

5.3.2.2 Figure 15: Vapour concentration versus downwind distance. Figure 15 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 15, the weather condition must be determined from Table 7.

Use: The maximum hazard distance, X_p , downwind of the spill can be calculated from Figure 15 knowing:

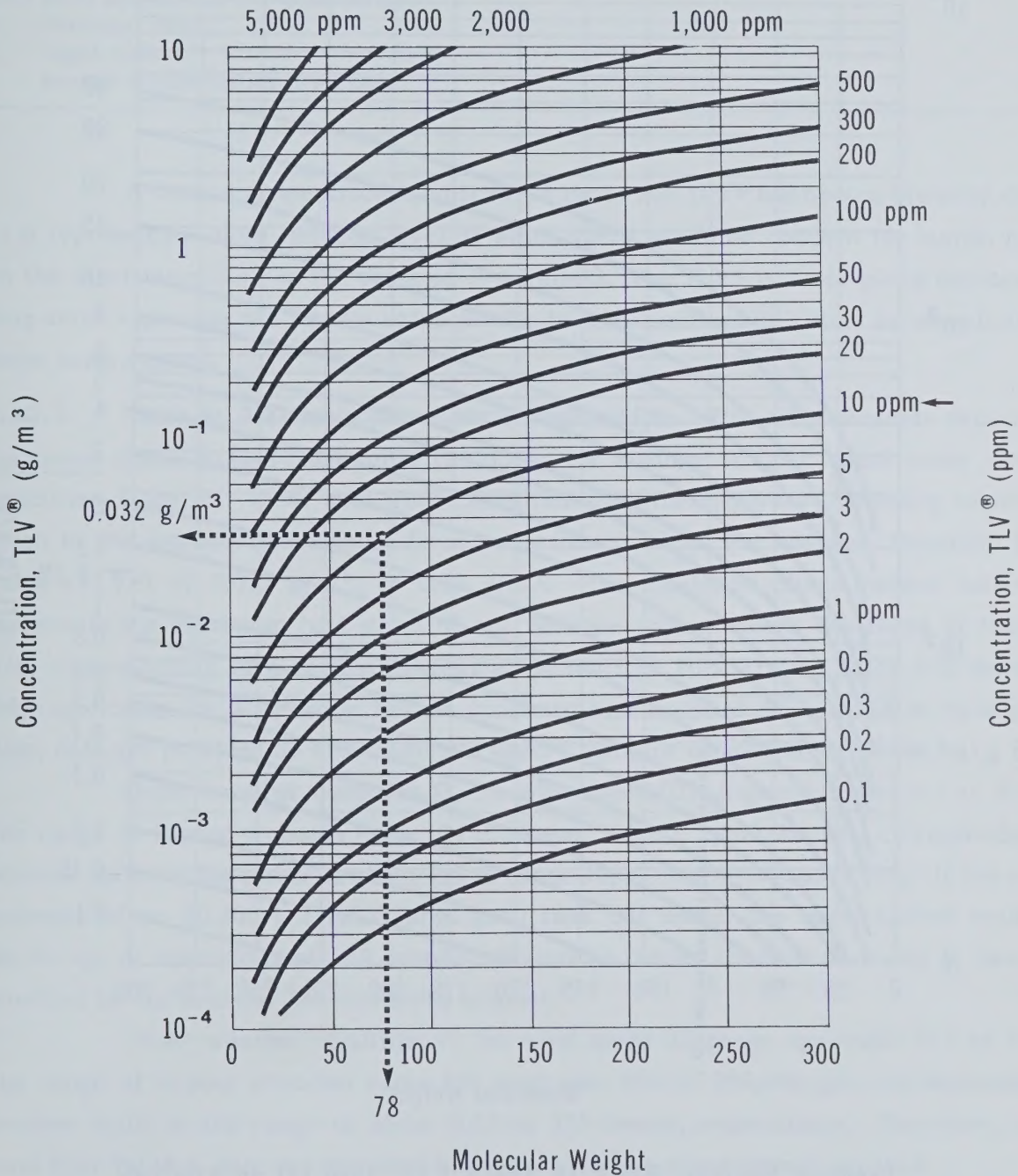
- Q , the vapour emission rate (g/s)
- U , the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C , which is the lower value of 10 times the Threshold Limit Value* (TLV in g/m^3), or the Lower Flammability Limit (LFL in g/m^3). Note: To convert the TLV* (in ppm) and the LFL (in percent by volume) to concentrations in g/m^3 , use Figures 16 and 17.

BENZENE

NORMALIZED VAPOUR CONCENTRATION
VS DOWNWIND DISTANCE

BENZENE

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)

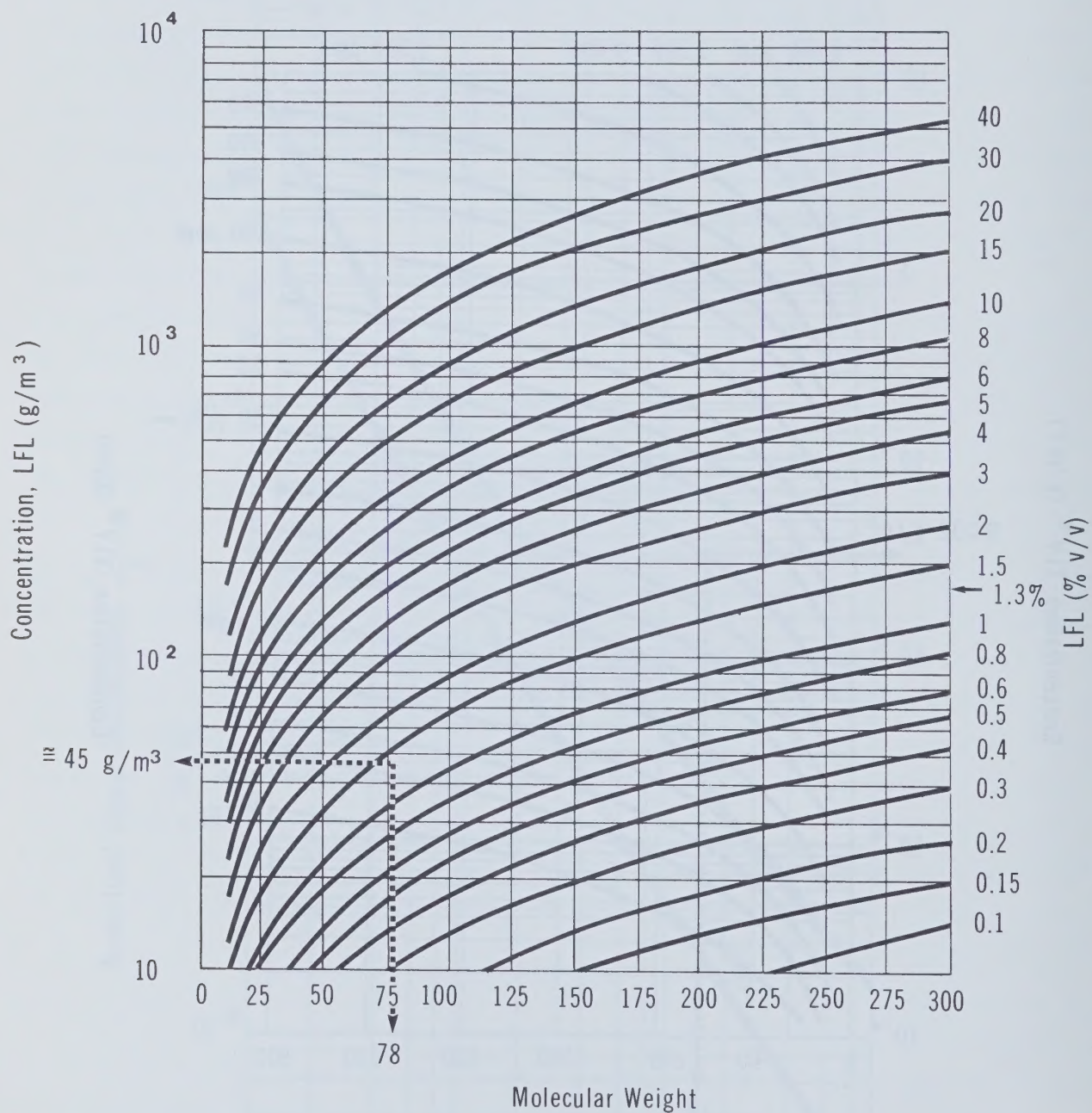


Example: Benzene, MW = 78, TLV® = 10 ppm, then TLV® in g/m³ ≈ 0.032

Note: data applicable at 25° and 760 mm Hg pressure

BENZENE

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example: Benzene, MW = 78, LFL = 1.3%, then LFL in g/m³ ≈ 45

Note: data applicable at 25°C and 760 mm Hg pressure

TABLE 7 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed <11 km/h (≈ 3 m/s) and one of the following: - overcast day - night time - severe temperature inversion	Most other weather conditions

A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure; use of this value as the hazard limit would result in unrealistically large hazard zones.

5.3.2.3 Table 8: Maximum plume hazard half-widths. This table presents data on the maximum plume hazard half-width, $(W/2)_{\max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the benzene Threshold Limit Value (TLV®) of 0.032 g/m^3 , or 0.32 g/m^3 . The maximum plume hazard half-width represents the maximum half-width of the benzene vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of $10 \times \text{TLV}^\circ$. Table 8 is therefore only applicable for a benzene hazard concentration limit of $10 \times \text{TLV}^\circ$ or 0.32 g/m^3 . Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 3000 to 2,000,000 g/s, corresponding to benzene spills in the range of about 0.3 to about 10,000 tonnes, respectively. If the entire contents of an 80,000 L (17,600 Imp. gal.) tank car spills, the mass spilled would be 70,300 kg, or approximately 70 tonnes. Therefore, under Class D of Table 8, data are provided for up to about 140 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 300 to 200,000 g/s, corresponding to benzene spills in the range of about 0.05 to 375 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 5 times a standard rail car load.

Use: Knowing the weather condition, Q and U , compute Q/U . Choose the closest Q/U value in the table and the corresponding $(W/2)_{\max}$, the maximum plume

TABLE 8 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR BENZENE AT 20°C)

Weather Condition D		Weather Condition F	
Q/U (g/m)	(W/2) _{max} (m)	Q/U (g/m)	(W/2) _{max} (m)
2,000,000	3,200 (99.5 km)*	200,000	1,480 (99.5 km)*
1,800,000	2,990	150,000	1,190
1,600,000	2,785	125,000	1,040
1,400,000	2,560	100,000	880
1,200,000	2,330	75,000	710
1,000,000	2,080	50,000	525
800,000	1,815	25,000	320
600,000	1,520	20,000	275 → (W/2) _{max} =275 m
500,000	1,360	15,000	230
400,000	1,180	10,000	180
300,000	990	5,000	115
250,000	885	2,000	65
200,000	770	1,000	40
150,000	645	500	30
100,000	510	100	10
75,000	430		
50,000	340		
25,000	230		
15,000	170		
5,000	90		
1,000	35		
500	25		
100	10		

* Data are provided up to a maximum downwind hazard distance of 100 km.

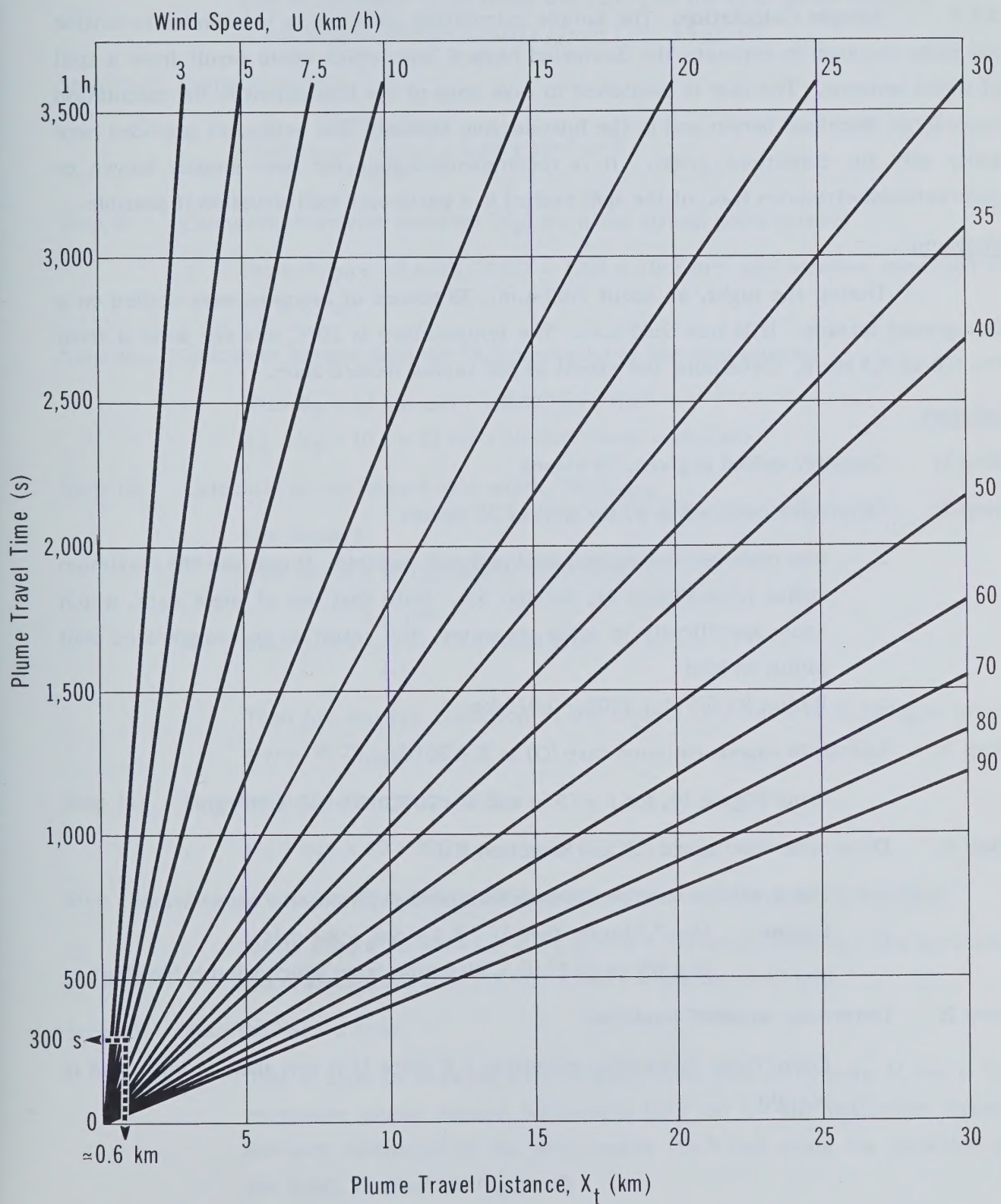
Example: A spill releasing benzene vapour at the rate of $Q = 4 \times 10^4$ g/s under weather condition F and a wind speed $U = 2.1$ m/s means $Q/U = 19,050$ g/m, which results in a maximum plume hazard half-width $(W/2)_{\max} = 275$ m.

Note: Above table is valid only for a benzene concentration of $10 \times \text{TLV}^{\circ}$, or 0.32 g/m³.

hazard half-width, in metres. (For numbers not shown, interpolate Q/U and $(W/2)_{\max}$ values.) Also refer to the example at the bottom of Table 8.

5.3.2.4 Figure 18: Plume travel time versus travel distance. Figure 18 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

BENZENE

PLUME TRAVEL TIME
VS TRAVEL DISTANCE

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined; it indicates how far downwind the plume has travelled.

5.3.3 Sample Calculation. The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid benzene. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill radius) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of benzene were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution

Step 1: Quantity spilled is given, 20 tonnes

Step 2: Determine pool radius (r) for spill of 20 tonnes

- Use observed (measured) pool radius if possible. If not, use the maximum radius from Figure 21, Section 5.4. Note that use of these data, which apply specifically to spills on water, will result in an exaggerated pool radius on land
- Radius (r) $75 \text{ m} \div 1000 = 0.075 \text{ km}$

Step 3: Calculate vapour emission rate (Q) at $T = 20^\circ\text{C}$

- From Figure 14, for $r = 75 \text{ m}$ and $T = 20^\circ\text{C}$, $Q = 4.0 \times 10^4 \text{ g/s}$

Step 4: Determine wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given: $U = 7.5 \text{ km/h}$, then $U = 7.5 \div 3.6 = 2.1 \text{ m/s}$
 $D = \text{NW or } 315^\circ$ ($D = \text{Direction from which wind is blowing}$)

Step 5: Determine weather condition

- From Table 7, weather condition = F since U is less than 11 km/h and it is night

Step 6: Determine hazard concentration limit (C)

- This is the lower of 10 times the TLV[®], or the LFL, so for benzene
 $C = 0.32 \text{ g/m}^3$ (TLV[®] = 0.032 g/m^3 ; LFL 45 g/m^3)

Step 7: Compute CU/Q

- $$\text{CU/Q} = \frac{0.32 \times 2.1}{4 \times 10^4} = 1.68 \times 10^{-5} \text{ m}^{-2}$$

Step 8: Calculate downwind distance (X_p) from the virtual point source.

- From Figure 15 with $\text{CU/Q} = 1.68 \times 10^{-5} \text{ m}^{-2}$ and weather condition F,
 $X_p \approx 15 \text{ km}$

Step 9: Calculate hazard distance (X_a) downwind of the area source

- With $X_p = 15 \text{ km}$ and $r = 0.075 \text{ km}$, then
 $X_a = X_p - 10 r = 15 \text{ km} - 10 (0.075 \text{ km}) = 14.3 \text{ km}$

Step 10: Calculate plume hazard half-width, $(W/2)_{\max}$

- Use Table 8
- With $Q = 4 \times 10^4 \text{ g/s}$ and $U = 2.1 \text{ m/s}$

$$\text{then } Q/U = \frac{4 \times 10^4}{2.1} = 19,050 \text{ g/m}$$

- Then for weather condition F, the closest Q/U value is $20,000 \text{ g/m}$ which gives $(W/2)_{\max} \approx 275 \text{ m}$

Step 11: Determine the time since spill

- $t = 5 \text{ min} \times 60 = 300 \text{ s}$

Step 12: Calculate distance travelled (X_t) by vapour plume since time of accident

- Using Figure 18 with $t = 300 \text{ s}$ and $U = 7.5 \text{ km/h}$, then $X_t = 0.6 \text{ km}$ (more accurately from $U t = 2.1 \text{ m/s} \times 300 \text{ s} = 630 \text{ m} = 0.63 \text{ km}$)

Step 13: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (275 m) by the maximum hazard distance downwind of the area source (14.3 km) along the direction of the wind, as shown in Figure 19

- If the wind is reported to be fluctuating by 20° about 315° (or from $315^\circ \pm 10^\circ$), the hazard zone is defined as shown in Figure 20
- Note that the plume has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 115 minutes before the plume reaches the maximum downwind hazard distance of 14.3 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on water, benzene will spread on the surface. Because it is only slightly soluble, a very small amount will be dissolved in the water; the rest will evaporate until it is removed. The evaporation occurs very rapidly and thus movement on rivers, etc., is not a relevant concern in most situations.

For the purpose of nomogram preparation, the extent of spread on the surface of the water has been estimated, assuming that none of the benzene is dissolved in the water. However, the loss due to evaporation has been taken into account.

The rate of spreading on water is based on the balance of forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces). The maximum size of the spill pool depends to a large extent on the rate of evaporation.

The equations representing the spreading of the spill on water are presented in the Introduction Manual. In the nomogram presented, the water temperature is assumed to be 20°C , representing a reasonable maximum for surface water bodies. This condition maximizes the spill size.

5.4.2 Nomogram for Spreading on Still Water. The following nomogram (Figure 21) simplifies the estimation of the spreading of benzene on still water (with no dissolution) and of the time for complete evaporation for a range of spill sizes. Assuming no dissolution in water, Figure 21 provides a simple means of estimating the maximum spill radius for benzene, if the spill mass is known. The nomogram is based on data presented in the Hazard Assessment Handbook (CHRIS 1974) and a computer model for simultaneous spreading and evaporation of a cryogenic liquid spilled on water (Raj 1974). The bracketed figures on the nomogram provide an estimate of time for complete evaporation of the spill. Because of the short times involved, the complete time history of the spread of the spill has not been considered. Similarly, the translation distance of the spill by wind or surface current is not considered.

BENZENE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

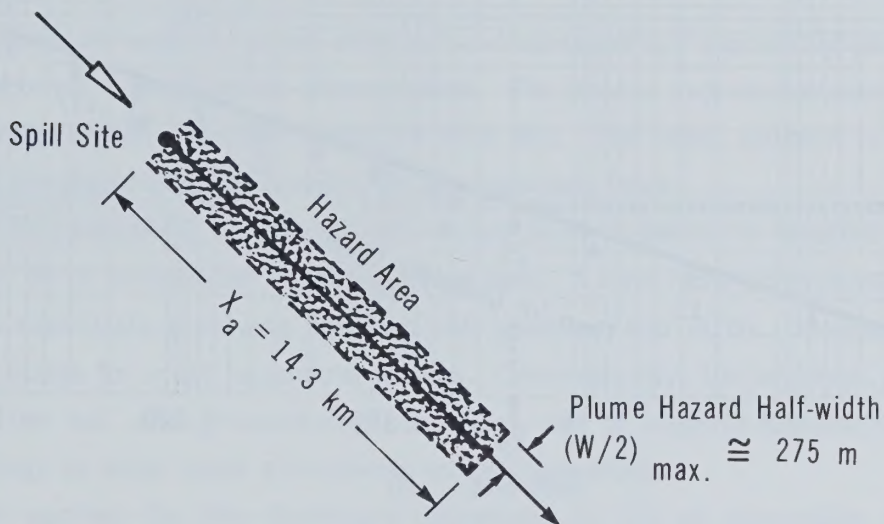
Wind $U = 7.5$ km/h from 315° (NW)

FIGURE 20

BENZENE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM

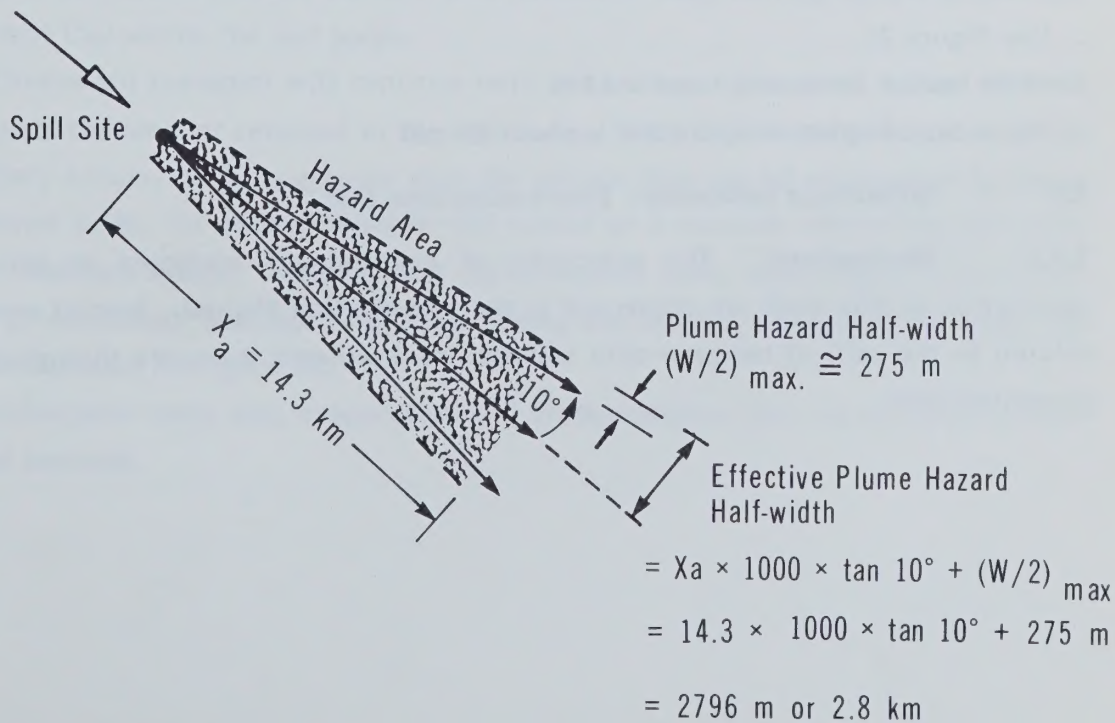
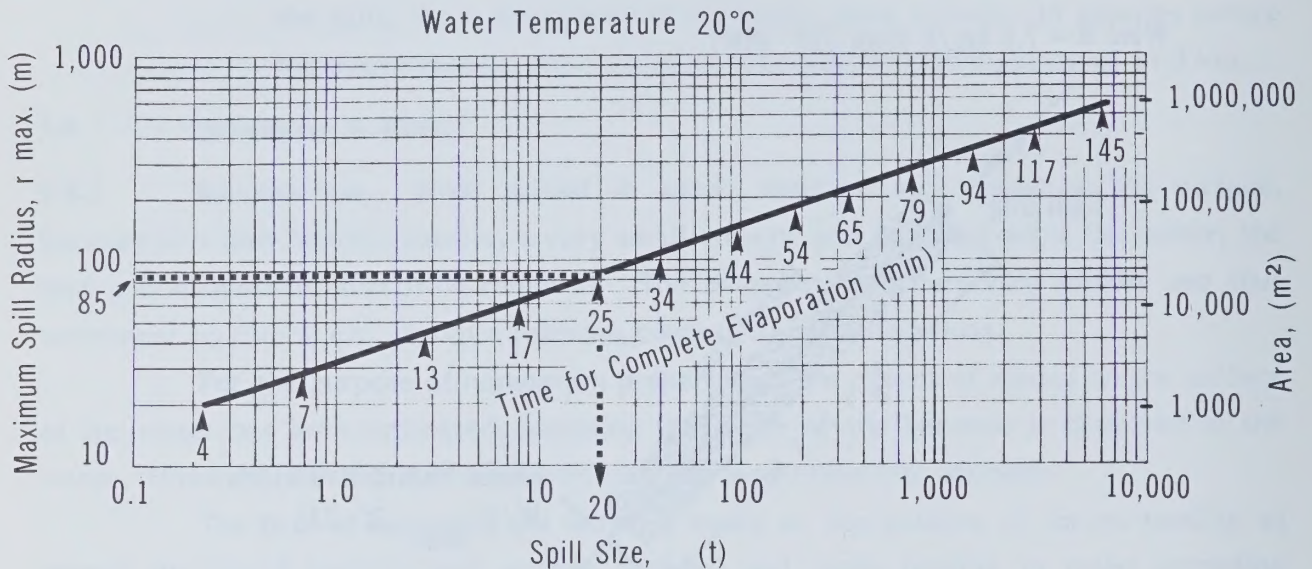
Wind $U = 7.5$ km/h from $315^\circ \pm 10^\circ$ 

FIGURE 21

BENZENE

MAXIMUM SPILL RADIUS
VS SPILL SIZE

5.4.3 Sample Calculation. A 20 tonne spill of benzene has occurred on a large lake. What is the maximum size of the spill (assuming no dissolution) and approximate time for complete evaporation?

Solution

- Use Figure 21
- With mass = 20 tonnes, $r_{max} = 85$ m
- Time for complete evaporation is about 25 min

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of benzene onto soil and its downward transport through the soil are presented here.

Benzene has a boiling point of 80.1°C at a pressure of 1 atmosphere. When spilled onto soil below that temperature, limited evaporation will occur. Evaporation from a pool at 20°C occurs at a rate of $2.3 \text{ g}/(\text{m}^2\cdot\text{s})$. The remaining benzene will infiltrate the soil. Once all the benzene has penetrated the soil, evaporation continues at a reduced rate.

When benzene is spilled onto soil and subsequently exposed to precipitation, its transport becomes a multi-phase phenomenon. The phases include benzene and water as liquids and vapours, and benzene adsorbed onto soil. The main concern is the downward transport of the liquid benzene toward the groundwater table.

Unfortunately, sufficient data do not exist to permit a detailed assessment of the transport of an immiscible contaminant in soil. A few field investigations have been carried out, especially involving spills of oil, gasoline and PCBs. However, very little information exists for most hazardous wastes. Consequently, for benzene, it is necessary to simplify the soil and groundwater conditions and to express contaminant behaviour through analogy to other more extensively studied materials.

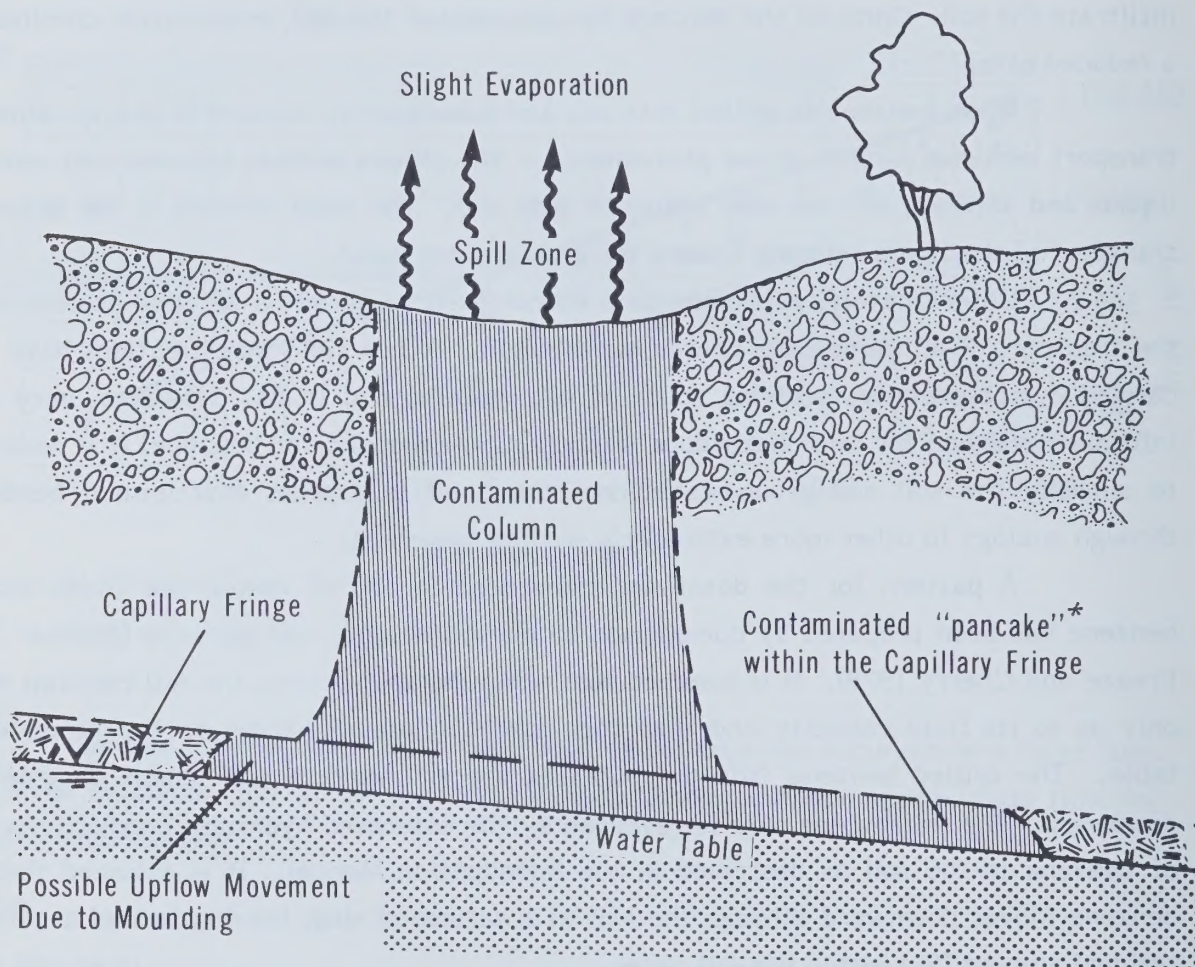
A pattern for the downward movement in soil of immiscible fluids such as benzene has been prepared by comparison to oil spilled onto soil surfaces (Blokkeer 1971; Freeze and Cherry 1979). It is assumed that when the spill occurs, the soil contains water only up to its field capacity and that this condition prevails down to the groundwater table. The spilled benzene fills the pores at the soil surface and begins to penetrate downward. The infiltration rate is governed by the saturated hydraulic conductivity (K_0) of benzene in the soil as described in the Introduction Manual. It is assumed that the benzene moves downward through the soil as a saturated slug, leaving behind a constant residual amount (S_0) within the soil pores.

Downward transport will continue until the volume of benzene spilled per unit area (B_0) equals the amount retained in the soil as S_0 . Some lateral spreading may occur due to capillary action. If B_0 is greater than the volume that can be retained as S_0 above the groundwater table, the excess benzene will spread as a pancake within the saturated groundwater capillary fringe. The resultant contaminated zone, consisting of a "vertical" column and a "horizontal" pancake of soil containing the residual amount of benzene, S_0 , is shown schematically in Figure 22.

Adsorption onto soil, evaporation and biodegradation can influence the subsequent fate of benzene.

BENZENE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

* Column and Pancake Contain Residual Benzene, $S_0 = 0.05$

5.5.2 Equations Describing Benzene Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table are described in the Introduction Manual. Transport velocities are based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Benzene in Soil. The saturated hydraulic conductivity (K_0), in m/s, is given by:

$$K_0 = \frac{(\rho g)k}{\mu}$$

where: k = intrinsic permeability of the soil (m^2)
 ρ = mass density of the fluid (kg/m^3)
 μ = absolute viscosity of the fluid ($Pa \cdot s$)
 g = acceleration due to gravity = $9.81 m/s^2$

The fluids involved are benzene and water.

Property	Benzene		Water 20°C
	20°C	6°C	
Mass density (ρ), kg/m^3	879	890	998
Absolute viscosity (μ), $Pa \cdot s$	0.652×10^{-3}	0.84×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_0), m/s	$(1.32 \times 10^7)k$	$(1.04 \times 10^7)k$	$(0.98 \times 10^7)k$

5.5.4 Soils. The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

Property	Soil Type		
	Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fC}), m^3/m^3	0.075	0.3	0.45
Residual benzene in pores (S_0), m^3/m^2	0.05	0.1	0.2
Saturated hydraulic conductivity (K_0), m/s			
• 20°C	1.32×10^{-2}	1.32×10^{-5}	1.32×10^{-8}
• 6°C	1.04×10^{-2}	1.04×10^{-5}	1.04×10^{-8}

5.5.5 Penetration Nomograms. Nomograms were prepared for each soil showing the total depth of benzene penetration (B) versus penetration time (t_p) for various volumes spilled per unit area of soil (B_0). Temperatures of 6°C and 20°C were used. Calculations were based on the equations developed in the Introduction Manual.

A flow chart for using the nomograms is shown in Figure 23. The nomograms are presented in Figures 24, 25 and 26. The nomograms may be made to apply to spills of different magnitudes by multiplying both scales by the same factor.

	From Nomogram	Multiplier	New Values
$T = 20^\circ\text{C}$	$B_0 = 0.4 \text{ m}^3/\text{m}^2$	0.1	$B_0 = 0.04 \text{ m}^3/\text{m}^2$
Coarse sand	$t_p = 41 \text{ min}$	0.1	$t_p = 4.1 \text{ min}$
	$B = 23 \text{ m}$	0.1	$B = 2.3 \text{ m}$

5.5.6 Sample Calculation. A 20 tonne spill of benzene has occurred on coarse sandy soil. The temperature is 20°C; the spill radius is approximately 8.6 m. Calculate the depth and time of penetration and check the corresponding evaporation loss.

Solution

Step 1: Define parameters

- Mass spilled = 20,000 kg (20 tonnes)
- $T = 20^\circ\text{C}$
- Mass density $\rho = 879 \text{ kg/m}^3$
- $r = 8.6 \text{ m}$

Step 2: Calculate volume and area of spill

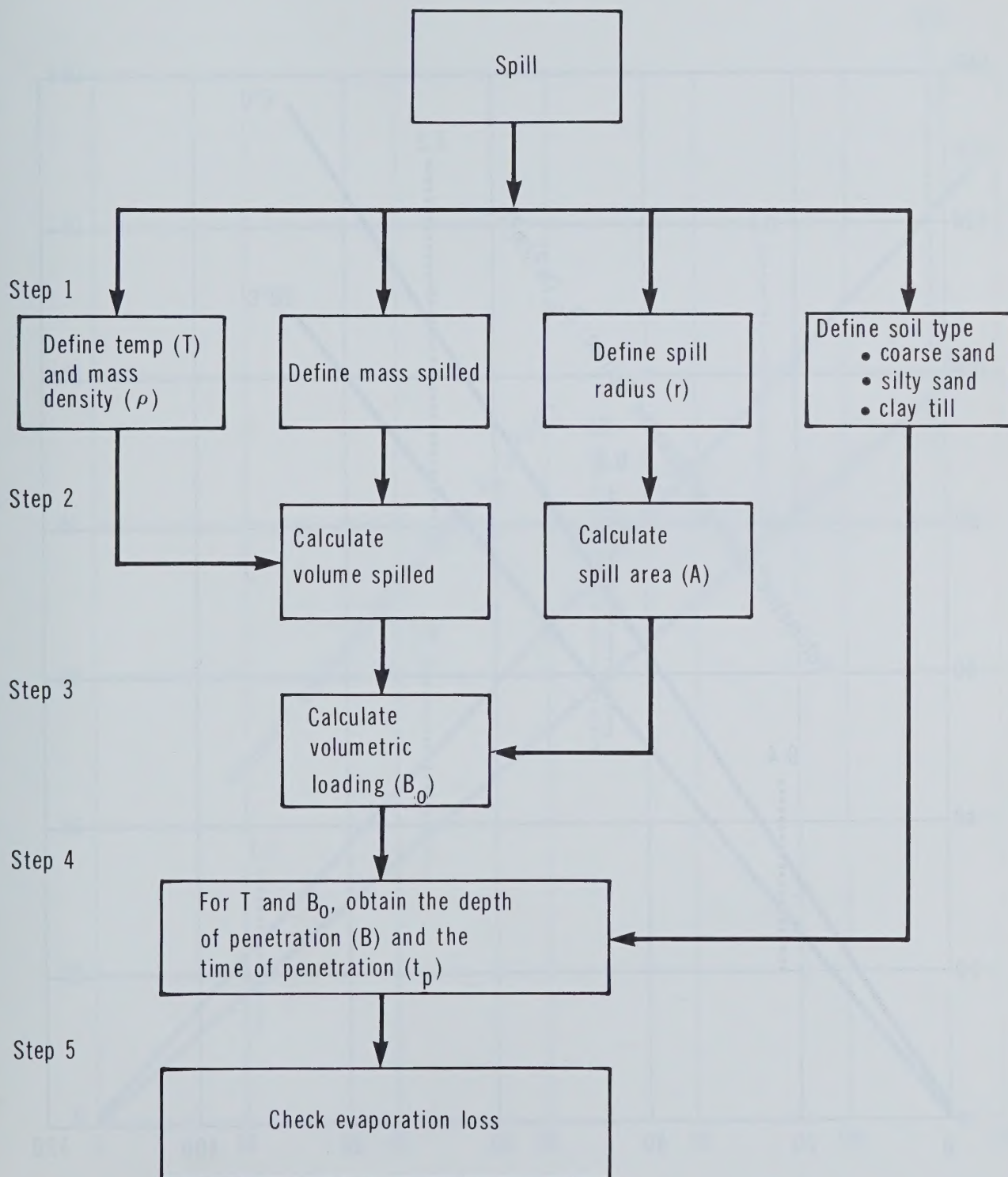
- $V = \frac{M}{\rho} = \frac{2 \times 10^4 \text{ kg}}{879 \text{ kg/m}^3} = 22.8 \text{ m}^3$
- $A = \pi r^2 = 232 \text{ m}^2$

Step 3: Calculate volumetric loading B_0

- $B_0 = \frac{V}{A} = \frac{22.8}{232} = 0.1 \text{ m}^3/\text{m}^2$

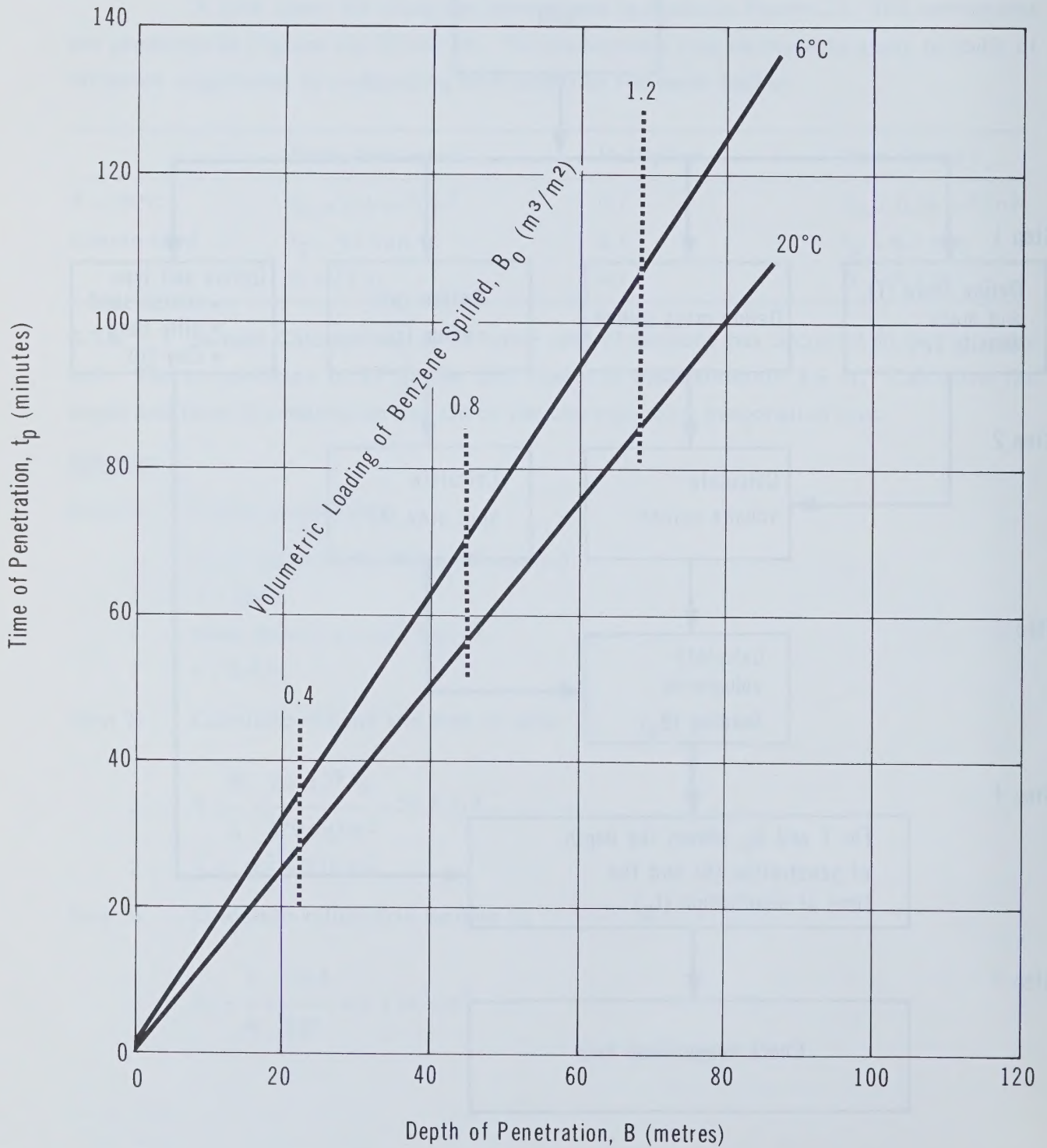
BENZENE

FLOWCHART FOR NOMOGRAM USE



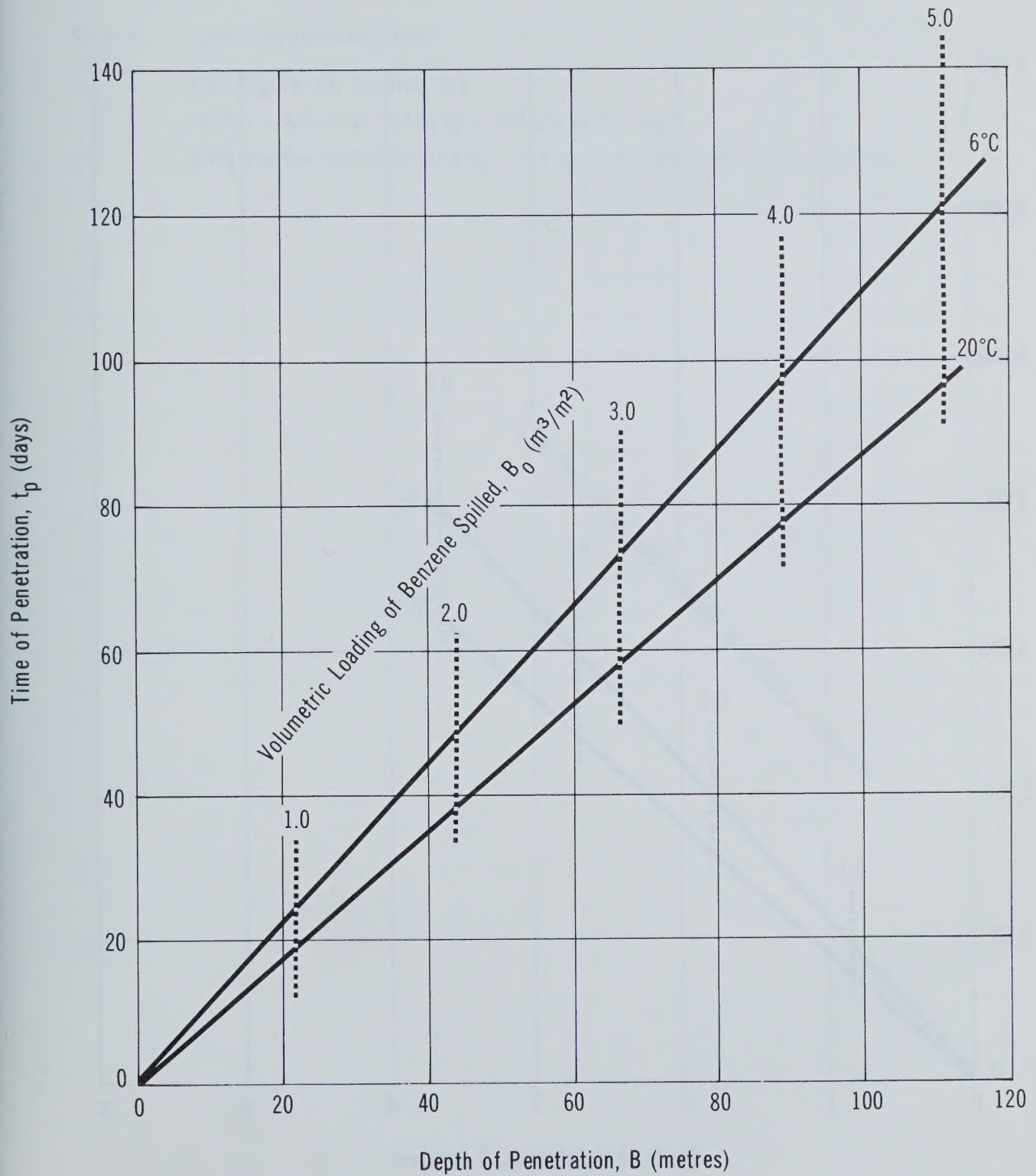
BENZENE

PENETRATION IN COARSE SAND



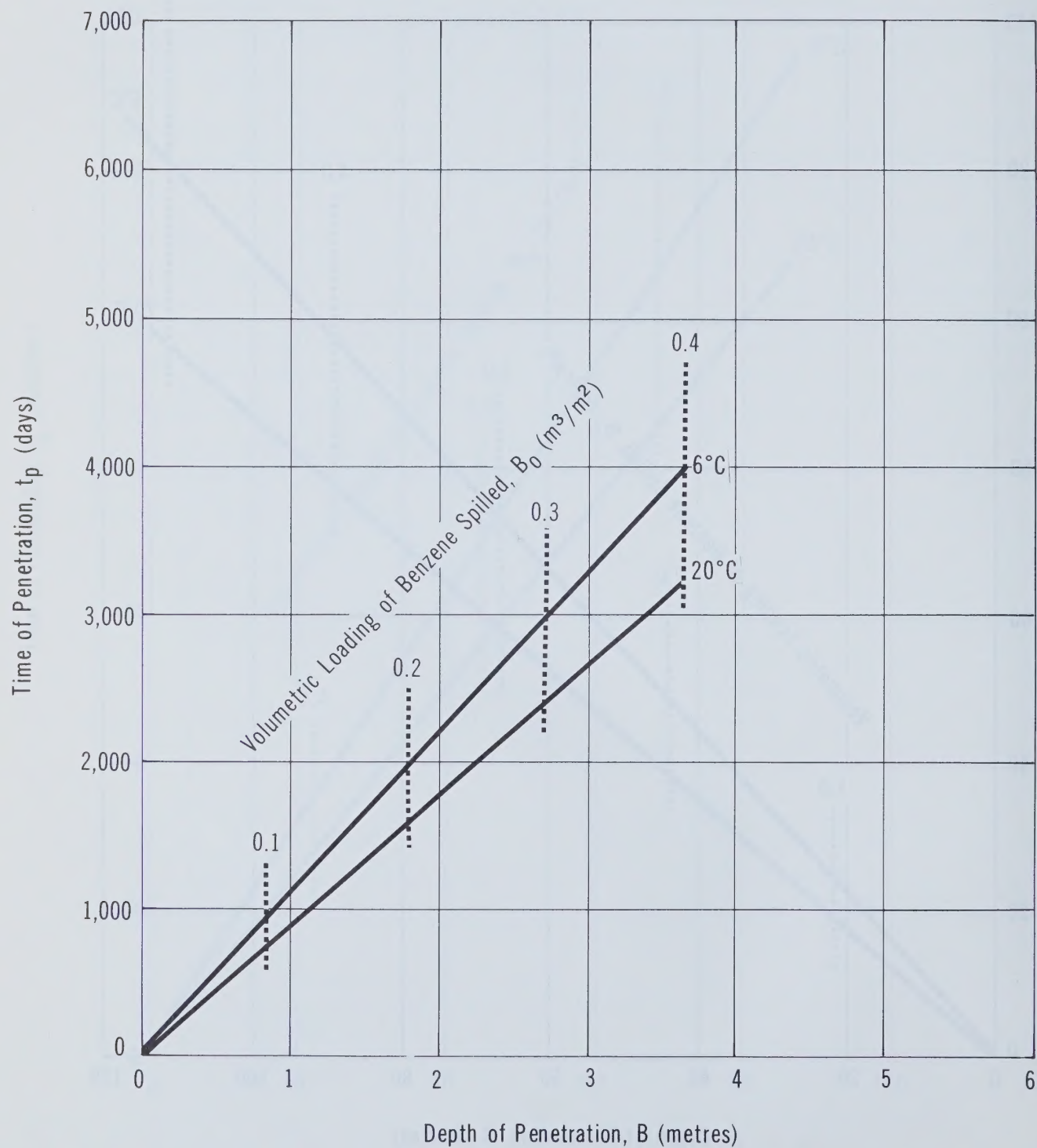
BENZENE

PENETRATION IN SILTY SAND



BENZENE

PENETRATION IN CLAY TILL



Step 4: Estimate depth of penetration (B) and time of penetration (t_p)

- For coarse sand, with $B_0 = 0.1 \text{ m}^3/\text{m}^2$
- $B = 6 \text{ m}$, $t_p = 7 \text{ min}$

Step 5: Check evaporation loss

- Use Figure 14, Section 5.3
- With $r = 8.6 \text{ m}$ at 20°C , $Q = 500 \text{ g/s}$ or 0.5 kg/s
- Evaporative loss (E) = $Q \times t_p = 0.5 \text{ kg/s} \times 7 \text{ min} \times 60 \text{ s/min} = 210 \text{ kg}$

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Benzene produces taste in water at levels of 0.5 to 4.5 mg/L. In chlorinated water, its taste level may be lower (EPA 440/9-75-009). The USSR has a recommended drinking water limit of 0.5 mg/L (Verschueren 1977).

6.1.2 Air.

6.1.2.1 Canada. Ontario has specified a limit of 10 mg/m³ of benzene in air (Ontario E.P. Act 1971). This limit applies to point source emissions when evaluated over a 30-minute period.

6.1.2.2 Other. The United States have proposed under the Clean Air Act (Section 112) that emissions of benzene from process vents of existing and new ethylbenzene and styrene plants be limited to 5 ppm by volume (Fed. Reg. 1980).

6.2 Aquatic Toxicity

6.2.1 Ontario. Benzene is moderately toxic to fish; in Ontario, it has been assigned a 96-h LC₅₀ of less than 100 mg/L (Water Management Goals 1978).

6.2.2 U.S. Toxicity Rating. Benzene has been assigned a TL_m96 (4-day median lethal toxicity rating) of 10 to 100 mg/L (RTECS 1979). The criterion to protect freshwater aquatic life is 3.1 mg/L as a 24-hour average and the concentration should not exceed 7 mg/L at any time (AWQC 1978). The criterion to protect saltwater aquatic life is 0.92 mg/L (24-hour average) and the concentration should not exceed 2.1 mg/L at any time (PTP 1980).

6.2.3 Measured Toxicities.

6.2.3.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Fish Toxicity Tests</u>					
9.2	96	Rainbow trout	LC ₅₀	12°C	Johnson 1980
425	96	Channel catfish	LC ₅₀	22°C	Johnson 1980
33	not stated	Minnows; carp	LC ₅₀	Golden Orfe test	Juhnke 1978

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
5.8 to 10.9	96	Bass (<i>M. saxatilis</i>)	LC ₅₀		TMAE 1978
33.5 to 35.5	24 to 96	Fathead minnow	TL _m	soft water	Verschueren 1977
24.4 to 32	24 to 96	Fathead minnow	TL _m	hard water	Verschueren 1977
6 to 7	6	Minnows	minimum lethal dose	hard water	Verschueren 1977
46	24	Goldfish	LD ₅₀		Verschueren 1977
386	96	Mosquito fish	LD ₅₀	tar & gas waste, dyeing & textile operations	WQCDB-1 1970
35 to 37	96	Sunfish	TL _m	tar & gas waste, dyeing & textile operations	WQCDB-1 1970
31 to 32	96	Bluegill; goldfish	TL _m		Pickering 1966
20	24 to 48	Bluegill	TL _m	tapwater; 20°C	WQC 1963

Conc. (mg/L)	Time (hours)	Species	Result	Reference
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Fish Kill Data

10	not stated	Trout	lethal	WQC 1963
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Toxicity Threshold (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
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Microorganisms

92	16	Bacteria	toxic, inhibits cell multi- plication	double dis- tilled water, 25°C	Bringmann 1980
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Toxicity Threshold (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
>1400	7 days	Green algae		double-dis-tilled water, 27°C, 50% relative humidity	Bringmann 1980
>700	72	Protozoa		double-dis-tilled water, 25°C	Bringmann 1980
525	48	Algae (<i>C. vulgaris</i>)	EC ₅₀ , 50% reduction in cell numbers		AWQC 1978

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Invertebrates</u>					
27	96	Shrimp	LC ₅₀		TMAE 1978
108	96	Crab larvae (stage 1)	LC ₅₀		TMAE 1978
178	48	<i>Daphnia magna</i>	EC ₅₀		AWQC 1978

6.2.3.2 Saltwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Fish Toxicity Tests</u>					
4.1	96	Striped bass	LC ₅₀		AWQC 1978
0.7	144	Pacific herring (eggs and larvae)	stress observed	Pacific waters	AWQC 1978
Up to 10	96	Young coho salmon	no significant mortality	artificial seawater	Verschuere 1977
20 to 25	48	Northern anchovy (larvae)	LC ₅₀	Pacific waters	Struhsaker 1974
20 to 25	48	Pacific herring (larvae)	LC ₅₀	Pacific waters	Struhsaker 1974

Conc. (mg/L)	Time (hours)	Species	Result	Reference
<u>Invertebrates</u>				
21	48	Brine shrimp	TL _m	Price, Waggy 1974
450	96	Copepod	LC ₅₀	AWQC 1978
27	96	Grass shrimp	LC ₅₀	AWQC 1978
108	96	Dungeness crab (larvae)	LC ₅₀	AWQC 1978
66	24	Brine shrimp	LC ₅₀	Price, Waggy 1974
<u>Marine Plants</u>				
>50	not stated	Dinoflagellate	growth inhibition	AWQC 1978
20	not stated	Diatom	growth inhibition	AWQC 1978
50	not stated	Algae	growth inhibition	AWQC 1978
60	96	Giant kelp	no effect on photo- synthetic activity	WQC 1963

6.3 Toxicity to Other Biota

6.3.1 Insects.

Conc. (mg/L)	Species	Result	Reference
59	Mosquito larvae (fourth instar)	LD ₅₀	NRC 1981
210	Grain weevils	LD ₅₀	NRC 1981

6.3.2 Livestock Studies. A maximum concentration of 0.25 mg/L of benzene found in reservoir water (freshwater) produced no effect in mammals when administered on a chronic basis (WQCDB-1 1970).

6.4 Other Land and Air Toxicity

There is cycling of benzene between the atmosphere and water. Since benzene is moderately volatile and is somewhat soluble, it is reasonable to believe that it could be washed out of the atmosphere with rainfall and then evaporated back into the atmosphere, causing a continuous recycling between the two media (AWQC 1978).

The chief environmental effects of benzene are probably its promotion of photochemical air pollution, an effect also produced by other hydrocarbons (NRC 1981).

6.5 Effect Studies

6.5.1 Aquatic Organisms. Benzene has been demonstrated to adversely affect aquatic life. Reproductive impairment has been observed in fish at benzene concentrations well below the lethal levels. Benzene in the environment has been demonstrated to have deleterious effects at many levels of the food chain (PTP 1980).

From numerous studies, it has been generalized that nearly all of the adverse acute and chronic effects of benzene in freshwater organisms occur at concentrations above 20 mg/L (AWQC 1978).

Benzene in marine waters may interact synergistically with other water-soluble aromatic components, thus affecting aquatic life at lower concentrations (Struhsaker 1974).

6.5.2 Animals. Chronic toxic effects of benzene are not documented. There is no evidence from studies to suggest that irreversible or persistent tissue damage occurs following sublethal acute exposures (NRC 1981).

6.6 Degradation

6.6.1 Biological Degradation. Benzene is only slightly (0.1 percent) soluble in water, and has a lower density and a higher vapour pressure than water. Spills will generally result in a colourless slick on the water surface; most of the benzene will evaporate. The half-life of non-saturated solutions has been estimated at 37 minutes, due to evaporation; 62 percent will evaporate by the time maximum solubility is reached (MacKay and Walkoff 1973). The remaining dissolved portion is subject to limited biodegradation. Oxygen uptake is slow for several days (Ryckman 1966). Benzene-saturated water is capable of seriously retarding sewage digestion (EPA 440/9-75-009).

6.6.2 C.O.D. The C.O.D. is 0.82 kg/kg (EPA 12020).

6.6.3 B.O.D.

B.O.D. kg/kg	% Theoretical	Days	Seed	Reference
<1	24	5	sewage seed	Price, Waggy 1974
<1	29	20	sewage seed	Price, Waggy 1974
>1	58	5	acclimated sewage seed	Price, Waggy 1974
>1	80	20	acclimated sewage seed	Price, Waggy 1974

From the B.O.D. values, benzene may be expected to remain a problem unless cleaned up, diluted or subjected to evaporation (OHM-TADS 1981).

Benzene is also known to be oxidized by microorganisms, especially bacteria (Brown 1978).

6.7 Long-term Fate and Effects

Benzene may bioaccumulate in living organisms and appears to accumulate in animal tissues that exhibit a high lipid content or represent major metabolic sites such as liver and brain (AWQC 1978). Benzene and its aliphatic derivatives have been found to accumulate in fish to greater than 1000 times the ambient concentration in 48 hours (Water Management Goals 1978).

6.8 Soil

6.8.1 Soil Degradation of Material. Information on the persistence or transport of benzene in soil is lacking. Benzene is subject to degradation by soil microbes at various rates that depend on soil types and other environmental factors. Small quantities of benzene would be expected to evaporate from soils or be degraded rather quickly, depending on the concentration (NRC 1981).

7 HUMAN HEALTH

There is a considerable amount of information in the published literature concerning the toxicological effects of test animal inhalation exposures to benzene, as well as information dealing with both chronic and acute human inhalation exposures. The literature also deals with the effects of absorption of this chemical through the skin, for both humans and test animals. In addition, literature has been published on the teratogenic, mutagenic and carcinogenic effects of benzene. Benzene was included in the catalogue of chemicals listed in the Second Annual Report on Carcinogens (DHHS 1981), and has been reported in the EPA TSCA Inventory.

Research projects on the toxicology of benzene continue to be reported frequently in TOX TIPS (a summary of current research activity), including both acute and chronic inhalation studies in test animals. Published work on benzene has been reviewed recently (API 1977). The data summarized here are representative of information in the literature.

The toxicological data summarized here have been extracted from reliable standard reference sources and are representative of information in the literature. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits. The exposure standards for benzene are designed to minimize the chronic systemic effects of this chemical. Canadian provincial guidelines generally are similar to those of USA-ACGIH unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
<u>Time-weighted Averages (TWA)</u>			
TLV® (8 h)	USA-ACGIH	10 ppm (30 mg/m ³)	TLV 1983
PEL (8 h)	USA-OSHA	10 ppm (skin)	GE 1978
MAC	-	100 ppm	AAR 1981
	USSR	1.5 ppm (5 mg/m ³)	Verschuere 1977
	Sweden	10 ppm	Doc. TLV 1981
	Czech.	16 ppm	Doc. TLV 1981

Guideline (Time)	Origin	Recommended Level	Reference
<u>Short-term Exposure Limits (STEL)</u>			
STEL (15 min)	USA-ACGIH	25 ppm (75 mg/m ³)	TLV 1983
Ceiling	USA-OSHA	25 ppm	GE 1978
Peak (10 min)	USA-OSHA	50 ppm	GE 1978
MIC (20 min)	USSR	0.48 ppm (1.5 mg/m ³)	Verschueren 1977
MIC (30 min)	Romania	0.75 ppm (2.4 mg/m ³)	Verschueren 1977
STIL* (30 min)		75 ppm	CHRIS 1978
<u>Other Human Toxicities</u>			
IDLH	USA-NIOSH	2,000 ppm	NIOSH Guide 1978
LD _{LO} (5 min)		20,000 ppm	Cheremisinoff 1979
TC _{LO} , severe (1 h)		1,500 ppm	AAR 1981
TC _{LO}		210 ppm	Cheremisinoff 1979
TC _{LO} (10 yr)		100 ppm	RTECS 1979
TD _{LO}		130 mg/kg	Sax 1981

* STIL - Short-term Inhalation Limit

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows:

$$ITI = 1315.12 (\text{Vapour Pressure in mm Hg}) / \text{TLV}^* \text{ in ppm}$$

$$ITI = 1315.12 (100 \text{ mm Hg @ } 26^\circ\text{C}/10)$$

$$ITI = 1.3 \times 10^4$$

Because the ITI is a measure of vapour toxicity, it cannot accommodate information pertaining to the toxicity of dusts, solids or aerosols.

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Arms or whole bodies subjected to cotton soaked with benzene (20 to 30 min)	No observable change in urinary inorganic sulphate to total sulphate ratio	Cesaro 1946. <u>IN NIOSH 1974</u>
SPECIES: Rabbit		
Undiluted (10 to 20 applications)	Slight to moderate irritation, moderate necrosis	Patty 1981
25% in vaseline (2 times per week)	Tremors, excitement, cachexia	Patty 1981
15 mg (24 h)	Mild irritation	AAR 1981
SPECIES: Rat		
0.6 g/kg (4 h/d for 4 mo)	Plasmic cell increase in bone marrow, disruption of erythropoietic element maturation	Patty 1981
SPECIES: Mouse		
1,232 mg/kg	TD _{LO}	AAR 1981
1,200 mg/kg (49 wk)	TD _{LO} , neoplastic effects	Sax 1981
48 mg/kg	TD _{LO}	AAR 1981
To cover dorsal skin of hairless mouse (2 yr)	Slightly above spontaneous frequency of several tumor types, but some skin papillomas	Patty 1981
2 μ L/application (3 times/d for 3 d)	Epidermal hyperplasia with neural invasion	Patty 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
88 mg (72 h)	Moderate irritation	AAR 1981
2 mg (24 h)	Severe irritation	Sax 1981
0.10 mL	Irritancy, moderate conjunctival irritant, causes transient corneal injury	Patty 1981
SPECIES: Rat		
50 ppm (600 h)	50% showed bilateral cataracts; however, cataracts not found in rats exposed for 750 h at 200 ppm	MOE 1978

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: gasoline-like odour, aromatic (AAR 1981)

Odour Index: 300 (AAR 1981)

Parameter	Media	Concentration	Reference
Odour Threshold	In air	3 to 5 ppm	CSC 1980
50% Response	In air	2.14 ppm	Little
100% Response	In air	4.68 ppm 0.875 ppm 0.042 ppm (vol.) and 0.13 µg/L, 1.5 ppm (vol.) and 4.8 µg/L	Little Cheremisinoff 1979 USDHEW 1967
Lower Threshold	In air	0.84 ppm	OHM-TADS 1981
Median Threshold	In air	31.3 ppm	OHM-TADS 1981
Upper Threshold	In air	53 ppm	OHM-TADS 1981
Recognition Odour Threshold	In air	180 mg/m ³ , 3.0 ppm, 4.68 ppm and 60 ppm	Sullivan 1969

Parameter	Media	Concentration	Reference
Threshold Odour Concentration	-	0.16 to 320 ppm	AAR 1981
Absolute Odour Threshold	-	0.160 ppm	AAR 1981
Median Recognition Threshold	-	11.8 ppm	AAR 1981
Upper Recognition Threshold	-	65.1 ppm	AAR 1981
Population Identification Threshold	-	2.14 to 4.68 ppm	AAR 1981

7.3.2 Taste.

Parameter	Media	Concentration	Reference
Lower Taste Threshold	-	0.5 ppm	OHM-TADS 1981

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Human		
20,000 ppm (5 min)	LD _{LO} , convulsions, paralysis, coma and death	Cheremisinoff 1979
7,500 (30 to 60 min)	Toxic effects	Flury 1928. <u>IN</u> NIOSH 1974
3,000 ppm (brief)	Eye and respiratory irritation	CSC 1980
3,000 ppm (30 to 60 min)	May be tolerated up to 1 hour	Patty 1981
1,500 ppm (1 h)	TC _{LO} , severe	AAR 1981
500 to 250 ppm	Nausea, drowsiness, and/or confused state of mind	Cheremisinoff 1979

Exposure Level (and Duration)	Effects	Reference
500 to 200 ppm	Vertigo, drowsiness, headache and nausea	CSC 1980
210 ppm	TC _{LO} , blood and toxic effects	Cheremisinoff 1979
200 to 100 ppm (8 h)	Urinary sulphate ratio below 40%	Doull 1980
100 ppm (5 h)	Average retention of 46% of inhaled benzene, elimination of 12% through lungs, 0.1-0.2% unmetabolized benzene in urine, 29% metabolized and excreted as phenol, 2.9% pyrocatechol and 1% hydroquinone	Teisinger 1952. <u>IN</u> NIOSH 1974
100 to 75 ppm (8 h)	Urinary sulphate ratio approximately 40%	Doull 1980
75 to 40 ppm (8 h)	Urinary sulphate ratio approximately 60%	Doull 1980
25 ppm (2 h)	Benzene concentration appears in the blood, clears within 300 min, no effect	Patty 1981
SPECIES: Primate		
Air saturated in benzene vapour	Ventricular extrasystole or periods of ventricular tachycardia which occasionally terminated in ventricular fibrillation	Patty 1981
SPECIES: Guinea Pig		
15,675 ppm (50 mg/L) (30 min)	Benzene blood level 8.0 mg/dL, 1.8 mg/100 mL phenol and clearing	Patty 1981
6,270 ppm (20 mg/L) (30 min)	Benzene blood level 3.2 mg/dL, 1.7 mg/100 mL phenol and clearing	Patty 1981
SPECIES: Rabbit		
35,000 to 45,000 ppm (3.7 min) (5.0 min) (6.5 min)	Light anesthesia Excitation and tremors Loss of pupillary reflex to strong light	Carpenter 1944. <u>IN</u> API 1977
(11.4 min)	Loss of blinking reflex to actual stimuli	
(12 min)	Pupillary contraction	
(15.6 min)	Involuntary blinking	
(36.2 min)	Death (range of 22 to 71 minutes)	
10,000 ppm	Death	Patty 1981

Exposure Level (and Duration)	Effects	Reference
10,000 ppm (2 h)	Benzene concentration in blood reached 25 to 30 mg/dL. Caused a decrease in RBC and an increase in the red cell resistance to saponin hemolysis	API 1977
4,000 ppm	Narcosis	Patty 1981
3,333 mg/m ³	LD ₅₀	OHM-TADS 1981
SPECIES: Dog		
45,800 ppm	Lethal dose	Patty 1981
SPECIES: Cat		
53,300 ppm	Lethal dose	Patty 1981
170,000 mg/m ³	LC _{LO}	AAR 1981
SPECIES: Rat		
Saturated vapour (5 min)	Lethal	AAR 1981
40,000 ppm (20 to 35 min)	3 of 8 male Long Evans rats died	Cheremisinoff 1979
16,000 ppm (4 h)	LD ₅₀	AAR 1981
13,700 ppm	LC ₅₀ , high level of liver and lung congestion	AAR 1981
10,000 ppm (7 h)	LD ₅₀	Cheremisinoff 1979
10,000 ppm (12.5 to 30 min)	2 of 10 male Long Evans rats died	Cheremisinoff 1979
10,000 ppm (up to 2 h)	Dyspnea, twitching of whiskers and ataxis, hyperreactivity to auditory stimuli, rigid tail and carpopedal spasms at 30 minutes, salivated profusely, cooler than normal skin	MOE 1978
SPECIES: Mouse		
60 mg/L (40 min)	Change in enzyme activity in spinal chord	Jonek 1965. IN API 1977
9,980 ppm	LC ₅₀	Patty 1981
2,195 ppm	Narcosis	Patty 1981

Exposure Level (and Duration)	Effects	Reference
<u>Chronic Exposures</u>		
SPECIES: Human		
5,320 ppm	60 of 184 workers suffering from chronic benzene poisoning, headaches, fatigue, exhaustion, bleeding of gums and nose, cutaneous hemorrhages in arms and legs, nervousness, vertigo, somnolence, smarting in eyes, palpitations, dyspeptic disorders, nausea, vomiting, loss of appetite and weight, itching and dermatitic changes	Helmer 1944. <u>IN NIOSH 1974</u>
2,100 mg/m ³	Toxic and carcinogenic effects	Cheremisinoff 1979
1,060 to 11 ppm (4 to 7 d/wk, 3 to 54 yr)	Lowest concentration: fatigue and dizziness. Medium concentration: fatigue, dryness of mucous membranes, hemorrhaging, nausea or vomiting and lethargy. Highest concentration: weakness, fatigue, epistaxis, dryness of mucous membranes, loss of appetite, nausea or vomiting, shortness of breath, dizziness, insomnia and lethargy	Patty 1981
660 to 190 ppm (4 yr)	Depression of the formed elements of the blood, myeloid metaplasia of the liver and spleen, death	Vigliani 1964. <u>IN NIOSH 1974</u>
650 to 150 ppm (4 mo to 15 yr)	Reversible pancytopenia, 28% thrombocytopenia, 14% macrocytic anemia, 3% megaloblastic erythropoiesis	Patty 1981
525 to 125 ppm	Some higher chromosome aberration in peripheral blood lymphocytes	Patty 1981
500 to 200 ppm	Development of leukemia in abnormal numbers of shoemakers	Cheremisinoff 1979
400 ppm (8 yr intermittently)	TC-ETA*	AAR 1981
210 to 30 ppm (3 mo to 17 yr)	Leukopenia 9.7%, pancytopenia 2.8%, eosinophilia 2.3%, thrombocytopenia 1.8%, basophilia 0.5%, giant platelets 0.5%; anemia was reversible	Patty 1981

Exposure Level (and Duration)	Effects	Reference
210 ppm	TC _{LO} , effects on all blood elements	Sax 1981
Greater than 200 ppm	Death	Doc. TLV 1981
105 ppm	Blood changes and one death	Doc. TLV 1981
100 ppm (10 yr)	TC _{LO} , central nervous system affected, toxic effects	RTECS 1979
100 ppm (work hours)	Leukopenia, headache, tiredness, breathlessness, 20% with some form of pancytopenia	Cheremisinoff 1979
100 ppm (10 yr)	Carcinogen	AAR 1981
60 ppm	Lowest value reported to cause a death	Doc. TLV 1981
25 ppm (work hours)	Lower hemoglobin levels, minor hematological deviations	Cheremisinoff 1979
SPECIES: Primate		
256 ppm (98 mg/m ³ , 8 h/d, 5 d/wk, 9 to 127 d)	Histopathology of all organs essentially negative, some slight weight reduction at the highest level	Patty 1981
SPECIES: Guinea Pig		
817 ppm (8 h/d, 5 d/wk, 30 exposure days)	No change in leukocyte count, slight drop in WBC count	Jenkins 1970. <u>IN</u> API 1977
88 ppm (269 d)	Blood, bone marrow, spleen and testes histopathological alterations	Cheremisinoff 1979
88 ppm (23 exposures in 32 days)	Mild leukopenia	API 1977
88 to 80 ppm (6 mo)	Mild leukopenia, splenic and testicular degeneration	Wolf 1956. <u>IN</u> API 1977
7 and 30 ppm (8 h/d, 5 d/wk, 9-127 d)	Histopathology of all organs essentially negative, some slight weight reduction at the highest level	Patty 1981
SPECIES: Rabbit		
12,000 ppm (1 h/d, several d)	Development of grayish white cornea, transient but persistent irritation	Patty 1981

Exposure Level (and Duration)	Effects	Reference
3,000 ppm (40 d)	Leukopenia	API 1977
88 to 80 ppm (6 mo)	Mild leukopenia, splenic and testicular degeneration	Wolf 1956. <u>IN</u> API 1977
80 ppm (175 d)	Leukopenia	API 1977
80 ppm (243 d)	Leukopenia and degeneration of seminiferous tubules	Cheremisinoff 1979
15.6 ppm	Decreased phagocytic index and phagocytic number	Cheremisinoff 1979
3.125 ppm (6 h/d, 14 d)	Hypertrophy of smooth endoplasmic reticulum, ribosome loss, disappearance of segmental distention of ergastoplasm, swelling and myelin degeneration of mitochondria	Cheremisinoff 1979
SPECIES: Dog		
1,100 to 750 ppm (4 to 110 wk, 5 to 8 h/d, 4 to 6 d/wk)	Leukopenia, decreased leukocyte count, death of 7 of 9 dogs tested	Jenkins 1970. <u>IN</u> API 1977
1,000 to 600 ppm (123 wk)	Leukopenia, shorter survival times	Hough 1944. <u>IN</u> API 1977
800 to 500 ppm (2 to 8 h/d, 24 to 410 d)	Base line benzene in blood increased from 5.0 to 6.5 times post exposure	Patty 1981
30 ppm (8 h/d, 5 d/wk, 9 to 127 d)	Histopathology of all organs essentially negative, some slight weight reduction at the highest level	Patty 1981
SPECIES: Cat		
Air saturated in benzene vapour	Ventricular extrasystole or periods of ventricular tachycardia which occasionally terminated in ventricular fibrillation	Patty 1981
SPECIES: Rat		
9,400 ppm (7 to 8 h/d, 5 d/wk, 6 mo)	Liver histopathology and bone marrow changes	Patty 1981
8,500 ppm (6 h/d, 10 d)	Enzymatic changes in peripheral blood leukocytes, reduction of lymphocytes, granular lymphocytes	Patty 1981

Exposure Level (and Duration)	Effects	Reference
6,600 ppm (7 to 8 h/d, 5 d/wk, 6 mo)	Liver histopathology and blood marrow changes	Patty 1981
4,400 ppm (7 to 8 h/d, 5 d/wk, 6 mo)	Narcosis and growth reduction	Patty 1981
2,200 ppm (7 to 8 h/d, 5 d/wk, 6 mo)	Narcosis and growth reduction	Patty 1981
1,650 ppm (6 h/d, 5 d/wk, 12 wk)	Leukopenia, partially reversed by phenobarbital	Patty 1981
1,000 ppm (23.5 h/d, 183 h)	Reduced white blood cell count, reduced DNA in bone marrow and increased red cell precursors	MOE 1978
1,000 ppm (23.5 h/d, 105 h)	Body weight loss, nose and mouth hemorrhage, stomach distention, engorged blood vessels, reversal of polymorphonuclear to lymphocyte ratio	Cheremisinoff 1979
1,000 ppm (7 h/d, 5 d/wk, 28 wk)	No central nervous system depression, good physical condition, leukocyte count nearly equal to initial value	Gofmekler 1968. <u>IN</u> API 1977
831 ppm (2 to 3 wk)	Significant leukopenia	Doull 1980
817 ppm (8 h/d, 5 d/wk, 30 exposure d)	Decreased leukocyte count, slight drop in white blood cell count	Jenkins 1970. <u>IN</u> API 1977
450 to 500 ppm (5 h/d, 10 d)	Increase in cytochrome P450 and aminopyrine demethylase activity	Cheremisinoff 1979
400 ppm (19 breaths/d, 36 d)	Peripheral blood showed slight anemia, leukocytosis thrombopenia, and reticulocytosis. Progressive depletion of myelopoietic cells in the bone marrow	Boje 1970. <u>IN</u> API 1977
400 ppm (13 wk)	Increased thrombocytes, leukopenia, decreased segmented granulocytes	Patty 1981
209.7 ppm 19.8 ppm 17.7 ppm 6.4 ppm 1.8 ppm 0.3 ppm (24 hours continuously before impregnation 10 to 15 d)	209.7 ppm - absence of pregnancy 19.8 ppm - 1/10 resorption of embryos observed The number of offspring per female was inversely related to the benzene concentration	Gofmekler 1968. <u>IN</u> API 1977

Exposure Level (and Duration)	Effects	Reference
200 ppm (8 h/d, 5 d/wk, 90 d)	Leukopenia	Cheremisinoff 1979
158 ppm (4 h/d)	Leukopenia and muscle antagonistic chronaxy	Cheremisinoff 1979
94 ppm (5.5 h/d, 30 d)	Increased α -aminobutyric acid level decreased in cerebellum but not mesencephalon, aspartic and glutamic acid decreased at both sites	Cheremisinoff 1979
88 ppm (136 ex- posures in 204 d)	Mild leukopenia in male rats	Wolf 1956. <u>IN</u> API 1977
88 ppm (204 d)	Blood, bone marrow, spleen and testes histopathological alterations	Cheremisinoff 1979
65 to 61 ppm (2 to 4 wk)	Leukopenia	Deichmann 1963. <u>IN</u> API 1977
47 to 44 ppm (5 to 8 wk)	Moderate but definite leukopenia	Deichmann 1963. <u>IN</u> API 1977
44 ppm (7 h/d, 5 d/wk, 5 to 7 wk)	Leukopenia in old adult rats and slight leukopenia in young adult rats	Cheremisinoff 1979
20 ppm (6 h/d, 6 d/wk, 5.5 m)	Delay in conditioned response time	MOE 1978
17 ppm (8 h/d, 5 d/wk, 9 to 127 d)	Histopathology of all organs essen- tially negative, some slight weight reduction at the highest level	Patty 1981
4.8 ppm continuous	Hyperplasia and vacuolization of smooth reticulum, selective des- truction of olfactory basal cells	Patty 1981
SPECIES: Mouse		
24 mg/L (6 h/d, 14 d)	Marked decrease in alkaline phos- phatase activity in liver	Jonek 1968. <u>IN</u> API 1977
24 mg/L (6 h/d, 14 d)	Liver slices showed changes in activity of succinate and lactate dehydrogenase G-6-phosphate dehy- drogenase and NADH-tetrazole reductase	Jonek 1969. <u>IN</u> API 1977
100 ppm (6 h/d, 20 d)	On 5th day decrease in spontaneous wheelturning	MOE 1978

* TC-ETA - Toxic Concentration - Equivocal Tumorigenic Agent

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
Species: Human		
130 mg/kg	TD _{LO} , central nervous system affected	Sax 1981
12 to 9 mg/kg	Staggering gait, vomiting, somnolence, shallow, rapid pulse, loss of consciousness, delirium, chemical pneumonitis, serious collapse and abrupt central nervous system depression	Patty 1981
SPECIES: Rabbit		
300 to 150 mg/kg	Use of cold and radioactive benzene had no effect	Patty 1981
SPECIES: Dog		
2.00 g/kg	Lowest reported lethal dose	Patty 1981
SPECIES: Rat		
5.6 g/kg	LD ₅₀	Cheremisinoff 1979
4.9 g/kg	LD ₅₀	Cheremisinoff 1979
3.8 g/kg	LD ₅₀	Sax 1981
3.4 g/kg	LD ₅₀ for a young adult	Cheremisinoff 1979
3.4 g/kg	LD ₅₀ and TC _{LO}	AAR 1981
3.0 g/kg	LD ₅₀	AAR 1981
5.6 mL/kg	LD ₅₀ ; hind limb paralysis, petechial bleeding in urinary tract, eyes and nose, mild gastritis and stripping of the epithelial lining of the glandular portion of the stomach of older adult rats	Withey 1975. <u>IN</u> API 1977
1.6 mL/kg (3 d)	Increased liver weight, decreased protein weight and enzyme activities	Patty 1981
1.0 mL/kg	LD ₅₀ for newborn rats	API 1977

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
4.7 g/kg	LD ₅₀	Cheremisinoff 1979
<u>Chronic Exposures</u>		
SPECIES: Guinea Pig		
1 mg/(kg·d) (6 mo)	Mild leukopenia, splenic and testicular degeneration	Gerarde 1956. <u>IN</u> API 1977
SPECIES: Rabbit		
1 mg/kg (6 mo)	Mild leukopenia, splenic and testicular degeneration	Patty 1981
SPECIES: Rat		
10,000 mg/kg (14 d)	LD ₅₀	AAR 1981
9.0 mg/kg plus 6.63 mg/m ³ (100 d)	Very rapid sensitizing and intoxicating effect (inhalation and ingestion combined)	Patty 1981
1.5 mg/kg plus 0.51 mg/m ³ (100 d)	Sensitizing in 30 to 40 days (inhalation and ingestion combined)	Patty 1981
250 mg/L plus 10 mg/m ³ (20 d)	Temporary changes in leukocyte counts and cholinesterase activity (inhalation and ingestion combined)	Patty 1981
250 mg/L (40 to 50 d)	Temporary changes in leukocyte counts and cholinesterase activity	Patty 1981
100 mg/(kg·d) (187 d)	Leukopenia and erythrocytopenia	Patty 1981
50 mg/(kg·d) (187 d)	Leukopenia and erythrocytopenia	Patty 1981
10 mg/(kg·d) (187 d)	Very slight leukopenia	Patty 1981
1 mg/(kg·d) (187 d)	No effect	Patty 1981
1 mg/(kg·d) (6 mo)	Mild leukopenia, splenic and testicular degeneration	Gerarde 1956. <u>IN</u> API 1977

7.4.3 Subcutaneous.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Guinea Pig		
530 mg/kg	Lowest lethal dose	Cheremisinoff 1979
0.527 g/kg	Lethal dose	Patty 1981
SPECIES: Rabbit		
2 mL/kg	Severe inhibition of DNA synthesis in bone marrow	Moeschlin 1967. <u>IN</u> API 1977
1 mL/kg	Depression in production of hemolysis agglutinins and opsonins	Simonds 1915. <u>IN</u> API 1977
1 mL/(kg·d)	Myeloid tissue was injured more than lymphadenoid tissue. Repeated injections ultimately rendered both tissues aplastic	Selling 1916. <u>IN</u> API 1977
0.5 mL/kg (every other day for 60 d)	Serum complement activity was reduced in proportion to the dose	Raddi 1963. <u>IN</u> API 1977
0.5 mL/(kg·d) (3 to 4 wk)	Decrease in blood leukocytes	Patty 1981
0.5 mL/(kg·d) (2 to 3 wk)	Decrease in peripheral blood leukocyte count, decreases in mitochondrial respiration	Patty 1981
0.5 mL/(kg·d)	Initial stimulation of pseudoeosinopoiesis, bone marrow promyelocyte and myelocyte count	Patty 1981
0.3 mL/(kg·d) (1 to 9 wk)	Pancytopenia, hypoplasia of bone marrow, with severe inhibition of the DNA synthesis	Patty 1981
0.2 mL/(kg·d)	Chromosomal aberrations (breaks and gaps) were present in bone marrow cells	Kissling 1972 <u>IN</u> API 1977
0.1 mL/(kg·d) (13 mo)	Increased pseudoeosinopoiesis	Patty 1981
0.05 to 0.1 mg/(kg·wk) (2 yr)	Autoantibodies rapidly appeared in plasma	Alekseeva 1969. <u>IN</u> API 1977
SPECIES: Rat		
1,150 mg/kg	LD ₅₀	Cheremisinoff 1979

Exposure Level (and Duration)	Effects	Reference
1 g/kg (12 d)	Chromosomal analysis at meta-phase: chromatid breaks 50.9%, gaps 44.7%, isochromatid breaks 4.34%	Patty 1981
200 mg/(kg·d) (12 d)	Chromosomal changes in bone marrow cells	Dobrokhtov 1972. <u>IN</u> API 1977
0.2 g/kg (12 d)	Lymphopenia, with toluene-increased neutrophils and bacillonuclear neutrophils	Patty 1981
1 to 2 mL/kg (3 wk)	Catalase activity decreased to 60 to 80% of control value in 10 days with sharp decline in 3 weeks	Hasegawa 1959. <u>IN</u> API 1977
2 mL/kg	Chromatid aberrations of chromosomes of bone marrow cells	Philip 1970. <u>IN</u> API 1977
2 mL/kg (21 d)	Cellular injury, mitochondrial swelling, severe dilation of membrane system, rough and smooth endoplasmic reticulum; severely disintegrated hematopoietic cells	Patty 1981
2 mL/(kg·d) (3 wk) or 1 mL/(kg·d) (5 wk)	Rapid decrease in femoral marrow nucleated cell count and DNA phosphorus % (of bone marrow dry weight)	Patty 1981
1 mL/(kg·d) (14 d)	Leukopenia, no significant change in hematocrit	Patty 1981
1 mL/kg	Reduced the production of specific precipitin and lysin	Hektoen 1916. <u>IN</u> API 1977
1 mL/kg (14 d)	Leukopenia	Gerarde 1966. <u>IN</u> API 1977
1 mL/kg (14 d)	Leukopenia with no significant change in hematocrit, involution of the spleen and thymus and a decrease in femoral marrow nucleated cell count and nucleic acid. The injury was reversible	Gerarde 1956. <u>IN</u> API 1977
SPECIES: Mouse		
2.20 g/kg	50% inhibition of circulatory erythrocytes	Patty 1981

Exposure Level (and Duration)	Effects	Reference
2,200 to 440 mg/kg	Depression of ^{59}Fe utilization was observed before a decrease in total leukocytes or hematocrit	Lee 1973. <u>IN</u> API 1977
600 mg/kg (17 wk)	TD _{LO} , ETA	Sax 1981
468 mg/kg	LD ₅₀	Cheremisinoff 1979
0.44 g/kg	27% inhibition of circulatory erythrocytes	Patty 1981
0.088 g/kg	No effect	Patty 1981
0.5 mL/kg (2 times/d, 1 to 10 d)	Dose-dependent binding to liver, residue increasing with time; initial binding to bone marrow, disassociation after day 6	Patty 1981

7.4.4 Intraperitoneal.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Guinea Pig		
0.01 mL, or 0.03 mL	Small dose (0.01 mL) benzene injected before injection of antigen elevated the reactivity to the second dose of antigen, whereas higher dose (0.03 mL) decreased this activity	Schiff 1914. <u>IN</u> API 1977
527 mg/kg	LD _{LO}	Sax 1981
SPECIES: Rat		
1,150 mg/kg	LD _{LO}	Sax 1981
SPECIES: Mouse		
990 µg/kg	LD ₅₀	RTECS 1979; AAR 1981; Sax 1981

7.4.5 Carcinogenicity, Mutagenicity and Teratogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
2,100 mg/m ³	Toxic and carcinogenic effects	Cheremisinoff 1979
525 to 125 ppm	Some higher chromosome aberrations in peripheral blood lymphocytes	Patty 1981
500 to 200 ppm	Development of leukemia in abnormal numbers of shoemakers	Cheremisinoff 1979
100 ppm (10 yr)	Carcinogen	AAR 1981
<10 ppm	Not a teratogenic hazard	Gulf 1981
SPECIES: Rabbit		
2 mL/kg	Severe inhibition of DNA synthesis in bone marrow	Moeschlin 1967. <u>IN</u> API 1977
0.3 mL/(kg·d) (1 to 9 wk)	Pancytopenia, hypoplasia of bone marrow, with severe inhibition of DNA synthesis	Patty 1981
0.2 mL/(kg·d) (18 wk)	Chromosomal aberrations (breaks and gaps) were present in bone marrow cells	Kissling 1972. <u>IN</u> API 1977
SPECIES: Rat		
2 mL/(kg·d) (3 wk) or 1 mL/(kg·d) (5 wk)	Rapid decrease in femoral marrow nucleated cell count and DNA phosphorus % (of bone marrow dry weight)	Patty 1981
1.23 to 0.71 g/kg	LD ₅₀ for pregnant rats	Cheremisinoff 1979
1 g/kg (12 d)	Chromosomal analysis at metaphase: chromatid breaks 50.9%, gaps 44.7%, isochromatid breaks 4.34%	Patty 1981
200 mg/(kg·d) (12 d)	Chromosomal changes in bone marrow cells	Dobrokhtov 1972. <u>IN</u> API 1977
1 mg/kg (12 d)	Chromosomal damage in 50.94% of bone marrow cells	Patty 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
3 mL/kg subcutaneous (5 d, 11 to 15 d of gestation)	Cleft palate, agnathia and micro- gnathia were observed more frequently in pregnant mice injected with benzene on 13th day of gestation	Watanabe 1970. <u>IN</u> API 1977
3,100 mg/m ³	Carcinogenic effects	Cheremisinoff 1979
2.70 g/kg	Found to be a teratogen	DHHS 1981
100 ppm (10 yr)	Carcinogen	AAR 1981
0.025 to 0.1 mL (54 wk, 104 wk)	Not a carcinogen	Patty 1981
0.015 to 0.06 mL (54 wk)	When sacrificed at 104th week, no leukemia was observed in C57BL/6N mice	Ward 1975. <u>IN</u> API 1977
0.001 mL (weekly until death)	No leukemogenic or aplastic effects were observed	Amiel 1960. <u>IN</u> API 1977
0.001 mL (weekly)	Developed "preleukemic" state in lymph nodes, spleen and liver	Hamaguti 1938. <u>IN</u> API 1977
0.001 mL (weekly)	6 of 20 treated high leukemia F strain mice developed leukemia, while 29 of 212 control also developed leukemia	Kirschbaum 1938. <u>IN</u> API 1977
0.001 mL in 0.1 mL olive oil (17 to 21 wk)	8 of 33 mice developed lympho- blastoma, leukemic or aplastic effect observed in AKR, DBA/Z, C3H and C57BL/6 mice	Lignac 1932. <u>IN</u> API 1977

7.5 Symptoms of Exposure

7.5.1 Inhalation.

1. Excitation, exhilaration, nervous energy (Cheremisinoff 1979).
2. Transient, mild irritation of respiratory and alimentary tracts (Patty 1981).
3. Headaches (Cheremisinoff 1979).
4. Tinnitus (Cheremisinoff 1979).
5. Insomnia, fatigue, irritability (Cheremisinoff 1979).
6. Nausea (Cheremisinoff 1979).

7. Anorexia (Cheremisinoff 1979).
8. Vertigo (Cheremisinoff 1979).
9. Depression (Cheremisinoff 1979).
10. Nose bleeds, bleeding gums, petechia, purpura, menorrhagia (Sax 1981).
11. Confusion (Sax 1979).
12. High colour index (Sax 1981).
13. Depletion of membrane transport enzymes (Patty 1981).
14. Blood abnormalities, including pancytopenia, red blood cell hemolysis, aplastic anemia, decreased hemoglobin levels, abnormal platelet function, macrocytosis, reticulocytosis, increased mean corpuscular volume, hyperbilirubinemia, leukemia, eosinophilia, basophilia, monocytosis and hyperplastic bone marrow effects (Cheremisinoff 1979; NIOSH 1974; Patty 1981; Sax 1979).
15. Splenomegaly, adenomegaly.
16. Chromosome aberrations (Cheremisinoff 1979).
17. Respiratory arrest (Patty 1981).
18. Convulsions (Cheremisinoff 1979).
19. Paralysis (Cheremisinoff 1979).
20. Loss of consciousness (Cheremisinoff 1979).
21. Death (Cheremisinoff 1979).

7.5.2 Ingestion.

1. Dizziness (Goodman 1980).
2. Weakness (Goodman 1980).
3. Headache (Goodman 1980).
4. Euphoria (Goodman 1980).
5. Blurred vision (Goodman 1980).
6. Irritation of mucous membranes of mouth, throat, esophagus and stomach (NIOSH 1974).
7. Nausea (Goodman 1980).
8. Vomiting (Goodman 1980).
9. Tremors (Goodman 1980).
10. Tightness in the chest (Goodman 1980).
11. Shallow rapid respiration (Goodman 1980).
12. Pneumonia (NIOSH 1974).
13. Bronchitis (NIOSH 1974).
14. Ventricular irregularities (Goodman 1980).
15. Paralysis (Goodman 1980).

16. Unconsciousness (Goodman 1980).
17. Death (Cheremisinoff 1979).

7.5.3 Skin Contact.

1. Erythema, blisters and scaly dermatitis (Cheremisinoff 1979).
2. Absorption may result in symptoms similar to those of inhalation exposure (AAR 1981).

7.5.4 Eye Contact.

1. Irritation (Cheremisinoff 1979).

7.6 Human Toxicity to Decay and Combustion Products

Benzene releases carbon monoxide and carbon dioxide on combustion (AAR 1981).

7.6.1 Carbon Monoxide and Carbon Dioxide. Carbon monoxide is a colourless, practically odourless gas which is a chemical asphyxiant. It causes hypoxia by complexing with hemoglobin and reducing the oxygen-carrying capacity of the blood. Excessive exposures will result in death from asphyxia. More moderate exposures may cause headaches and affect mental functions. The effects of moderate exposures are reversible, although considerable time is required to reverse the carbon monoxide-hemoglobin complexing reaction. The TLV® for carbon monoxide is 50 ppm (8 h-TWA) and 400 ppm (STEL) (Doc. TLV 1981).

Carbon dioxide is a colourless, odourless gas which in elevated concentrations may act to produce mild narcotic effects, respiratory stimulation, and asphyxiation. The TLV® for carbon dioxide is 5000 ppm (8 h - TWA) and 15,000 ppm (STEL) (Doc. TLV 1981).

8

CHEMICAL COMPATIBILITY

8.1 Compatibility of Benzene with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION OF GREATER TOXICITY	FORMATION OF TOXIC FUMES	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
<u>GENERAL</u>													
Heat	x											Highly flammable	Sax 1979
Fire	x	x										Moderate explosion hazard if benzene vapours are exposed to flame	Sax 1979
<u>SPECIFIC CHEMICALS</u>													
Bromine Pentafluoride	x	x											NFPA 1978
Chlorine		x										Explosion initiated by light	NFPA 1978
Chlorine Trifluoride		x						x				Can yield explosive reaction	NFPA 1978
Chromic Anhydride	x												NFPA 1978
Diborane	x	x											Bretherick 1979
Iodine Pentafluoride								x					Bretherick 1979

8.1 Compatibility of Benzene with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF VIOLENT POLYMERIZATION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION OF TOXIC FUMES	FORMATION OF GREATER TOXICITY PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Nitric Acid		x									Burning benzene will detonate on contact with concentrated nitric acid	Bretherick 1979
Nitryl Perchlorate		x									Reacts to give a slight explo- sion and flash	NFPA 1978
Oxygen (liquid)		x										NFPA 1978
Ozone		x		x							Forms formic, acetic, oxalic and other acids as well as an explosive called ozobenzene	NFPA 1978
Potassium Peroxide		x									Spontaneously flammable	NFPA 1978
Silver Perchlorate		x										NFPA 1978
Sodium Peroxide		x									Spontaneously flammable	NFPA 1978
Uranium Hexa- fluoride								x				Bretherick 1979
<u>CHEMICAL GROUPS</u>												
Strong Oxidizing Agents		x	x					x				EPA 600/2- 80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a review of the literature. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. These procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Benzene is a flammable liquid. The vapour forms explosive mixtures with air. Vapour may travel a considerable distance along the surface to distant ignition sources and flash back (NFPA 1978; GE 1978). It will react vigorously with strong oxidizers such as ozone, permanganates, sulphuric or nitric acids, potassium peroxide and sodium peroxide. Heating greatly increases the fire and explosion hazards. Oxidation in air will produce carbon monoxide and carbon dioxide (GE 1978).

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to help prevent rupture. Water may be ineffective for putting out the fire (NFPA 1978; GE 1978).

Small Fires: Dry chemical, CO₂, foam or water spray

Large Fires: Water spray, fog or foam

Move containers from fire area if this can be done without risk. Stay away from ends of tanks. For massive fire in cargo area, use unmanned hose holder or monitor nozzles (ERG 1980).

9.1.3 Spill Actions.

9.1.3.1 General. Stop discharge of material if this can be done without risk. Eliminate all sources of ignition. Use water spray to reduce vapours (ERG 1980). Avoid skin contact or inhalation (GE 1978). Application of fluorocarbon water foam to diminish vapours and provide wet down should also be considered (EPA 670/2-75-042).

Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area and the contents transferred to other suitable containers (MCA 1960). Benzene freezes at 5.5°C and thus may solidify if this action is taken.

Materials recommended for plugging leaks are polyester (Glad bag) and Imid polyester (brown-in-bag) (EPA 600/2-76-300). Other materials to be considered for leak

sealing are stafoam urethane foam, sea-going epoxy putty and MSA urethane (EPA 68-01-0106).

The following absorbent materials have shown possible applicability for vapour suppression and/or containment of benzene: cellosive and hycar (ICI 1982). It is recommended that combustible sorbents not be used if possible (CCPA 1982).

9.1.3.2 Spills on land. Contain if possible. Remove free liquid with explosion-proof equipment, soak up residue with sand, earth or vermiculite and shovel into metal containers which can be covered for disposal (ERG 1980; GE 1978). Application of fly ash or cement powder to absorb the liquid bulk should be considered. A universal gelling agent may be applied to immobilize the spill (EPA 670/2-75-042). Straw may also be used to absorb the slick (OHM-TADS 1981).

9.1.3.3 Spills on water. Contain if possible with booms or natural barriers to limit spreading. Use surface-acting agents to compress and thicken spilled materials. Remove trapped material with suction hoses (EPA 670/2-75-042). Straw may also be used to absorb the slick (OHM-TADS 1981). Caution must be used, however, with combustible sorbents of this type.

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills on land. After containment of benzene into a holding area, (oil) skimming equipment, sorbent foams or straw can be applied to remove the slick. Activated carbon may be used on the dissolved portion. Then remove trapped material for disposal (OHM-TADS 1981; CG-D-38-76).

9.1.4.2 Spills on water. After containment of spilled material with booms, (oil) skimming equipment, synthetic sorbent resins and straw can be applied to remove the slick (OHM-TADS 1981). Activated carbon can be applied at 10% the spill amount over the region occupied by 10 mg/L or greater concentrations. Mechanical dredges or lifts may be used to remove the carbon for disposal (EPA 670/2-75-042).

9.1.4.3 General. For treatment of contaminated water, gravity separation of solids followed by skimming of the surface to remove spilled material is recommended. If skimming is not sufficient, dual-media filtration followed by carbon adsorption should be considered. The recommended carbon ratio is 1.0 kg to 3.5 kg soluble material. The wastewater from backwash of the filtration and adsorption units is returned to the gravity separator (EPA 600/2-77-227).

The following treatment processes have shown possible applicability for spill countermeasures:

Process	% Removal (TSA 1980)	Process	Maximum % Removal (EPA 600/8-80-042E)
Biological	90 - 100	Clarification/Sedimentation	56
Stripping	95 - 99	Clarification/Sedimentation with Chemical Addition (Alum, Polymer)	
Solvent Extraction	97	Clarification/Sedimentation with Chemical Addition (Alum, Polymer)	> 97
		Clarification/Sedimentation with Chemical Addition (Alum, Lime)	50
		Granular Media Filtration	> 99
		Activated Sludge	> 99
		Lagoon (Aerated)	> 95
		Lagoon (Anaerobic)	50
		Solvent Extraction	97
		Granular Activated Carbon Adsorption	> 80
		Powdered Carbon Addition (with Activated Sludge)	95
		Reverse Osmosis	80

9.1.5 Disposal. Waste benzene must never be discharged directly into sewers or surface waters (MCA 1960; GE 1978). Incineration or disposal of benzene via a licensed solvent disposal company is recommended (GE 1978). Large quantities should be sent to a refinery for subsequent recovery. Small quantities may be mixed with earth or sand and then ignited (OHM-TADS 1981).

Following treatment either at the spill site or at a waste management facility, the resultant sludge can be disposed of at a secure landfill.

9.1.6 Charcoal Filtration Data (EPA 600/8-80-023). The following recommended values for the removal of benzene in water by either the single stage powdered carbon contactor or the granular carbon column adsorption system were obtained using the Freundlich Adsorption equation. The derivation of the equation is discussed in the Introduction Manual.

SINGLE STAGE POWDERED CARBON CONTACTOR SYSTEM

Initial Concentration (mg/L)	Carbon Doses (mg/L)	Final Concentration (mg/L)
1.0	35,000	0.1
1.0	> 100,000	0.01
0.1	> 100,000	0.001
0.1	> 100,000	0.01
0.1	> 100,000	0.001
0.01	> 100,000	0.001

GRANULAR CARBON COLUMN SYSTEM: (ESTIMATED)

Initial Concentration (mg/L)	Breakthrough Carbon Doses or Requirements (mg/L)
1.0	980
0.1	4,000
0.01	14,000

9.1.7 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be benzene:

- Safety goggles should be worn where spills and splashes to the eyes may occur; in those areas where facial sprays may occur, full-length shields (20 cm min. length) are required.
- When splashed on clothing that is permeable, the clothing should be removed immediately and laundered before reuse.
- In those workplaces where contact with the body is inevitable, impermeable clothing including boots, aprons, gloves, and sleeves should be worn.
- Neoprene is recommended as an impervious material (GE 1978).

- Eyewash stations and chemical safety showers should be readily available in areas of use and in spill situations.
- Spill personnel should wear an SCBA and impervious protective clothing (CCPA 1982).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where benzene is present (Cheremisinoff 1979).

Concentration of Benzene or Condition of Use	Recommended Respirator Usage for Various Benzene Concentrations Greater than 1 ppm
<u>< 10 ppm</u>	Chemical cartridge respirator with organic vapour cartridges and half mask. Any supplied-air respirator with half mask.
<u>< 50 ppm</u>	Chemical cartridge respirator with organic vapour cartridges and full facepiece. Any supplied-air respirator with full facepiece. Any organic vapour gas mask. Any self-contained breathing apparatus with full facepiece.
<u>< 1,000 ppm</u>	Supplied-air respirator with half mask in positive pressure mode.
<u>< 2,000 ppm</u>	Supplied-air respirator with full facepiece helmet or hood in positive pressure mode.
<u>< 10,000 ppm</u>	Supplied-air respirator and auxiliary self-contained breathing apparatus with full facepiece in positive pressure mode. Open-circuit self-contained breathing apparatus with full facepiece in positive pressure mode.
Entry into unknown concentrations or fire fighting	Open circuit self-contained breathing apparatus with full facepiece in positive pressure mode.
Escape only	Any organic vapour gas mask. Any self-contained breathing apparatus with full facepiece.

9.1.8 Special Precautions. Store containers away from heat, sources of ignition and oxidizing agents (GE 1978).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment, materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study.

Vapour suppressor	. National, Lorcon, Rockwood, 3M and MSA Foams
Recovery from water - floating materials	. Amine Carbamate Gelling Agent and Materials Application System
	. Lockheed Clean Sweep
	. Slickbar Slickskim Skimmers
Pumps for liquids	. Bell and Gossett (ITT) Centrifugal Pumps
Temporary storage	. Portable Collection Bag System
Removal from water	. EPA Mobile Physical-Chemical Treatment Trailers
Treating agents	. Hazorb (sorbent)
	. Petro-trap (sorbent)
	. Spill/Clean (gelling agent)

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

Although spills of this material have been recorded, no significant information regarding cleanup methods or response has been documented.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for analyses of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Benzene in Air

11.1.1 Gas Chromatography (NIOSH 1977). A range of 13 to 51.8 ppm benzene in air may be analyzed by gas chromatography (GC). This is currently the most practical method for identifying and measuring many volatile organic compounds. Retention time or Kovats index is used to identify the compound but positive identification requires the use of more than one column, special detectors, spiking the sample with the suspected component or combining GC with mass spectroscopy (MS).

A known volume of air is drawn through a glass sampling tube. The front section is packed with 100 mg of activated charcoal which is separated from 50 mg of charcoal in the back section by a 2 mm section of urethane foam. A 10 L air sample is recommended but this should be reduced if there is a large amount of benzene present. Maximum tube loading should be 16 mg. The sample is desorbed with 0.5 to 1.0 mL carbon disulphide. Desorption efficiency varies from 81 to 100 percent. Analysis is by GC with a flame ionization detector (FID), using a column packed with 50/80 mesh Porapak Q. In an alternative method, 10 percent FFAP on 80/100 AWD MCS chromosorb W is used (CCPA 1982). In high humidity, the condensation of water vapour reduces the collection

efficiency of the charcoal and the concentration of benzene may appear to be lower than it actually is. The loss of sample through overloading the charcoal tube may also produce lower results. An advantage of this method is that in the event of a mixed spill, two or more substances may be analyzed simultaneously.

Other sample collection methods may be useful in certain circumstances. A 1 L air sample may be collected and a 50 mL aliquot injected into a freeze-out trap at -80°C , packed with 20 percent Dow-Corning SF200 on 60/80 mesh columpak. Benzene is released by heating the trap to 100°C (Pilar 1973).

Alternately, the sample may be drawn through an adsorption tube packed with 300 mg of 80/100 mesh Porapak Q. The sample is thermally desorbed at 250°C directly into the GC (Baxter 1980). Advantages of these methods include the simplification of sample preparation and the elimination of solvent interference on the chromatogram.

Alternate columns are 10 percent carbowax on 80/100 mesh chromosorb W (ASTM 1981), 10 percent 1,2,3-tris(2-cyanoethoxy) propane on 100/200 mesh chromosorb PAW (Hester 1979), 1 percent OV-101 (or SE-30) on 100/120 mesh chromosorb W (Jones 1976; IERL 1976), and 30 percent N,N-Bis-2-cyanoethylformamide on 80/100 mesh pink support (Baxter 1980).

The use of a photoionization detector (PID) rather than a flame ionization detector (FID) allows analysis at the sub-ppm level without pre-concentration or trapping. Sample dilution may be necessary if the GC-PID is used as a vehicle-portable method and is transported to the spill site where the concentration may exceed the range of the detector (Hester 1979). Detectors using infrared absorption, with carbon monoxide or carbon dioxide lasers as sources, have a detection limit of 3 ppb for benzene (Kreuzer 1972).

11.2 Qualitative Method for the Detection of Benzene in Air

Air is drawn through a glass sampling tube as in Section 11.1.1. The sample is desorbed with chloroform and identified using the Friedel-Crafts alkylation reaction. Anhydrous aluminum chloride (about 100 mg) is placed in a test tube and heated until it sublimes. When it has cooled, a drop of the extract and two drops of chloroform are added with shaking. The appearance of an orange-red colour indicates the presence of an aromatic ring (Owen 1969).

11.3 Quantitative Methods for the Detection of Benzene in Water

11.3.1 Gas Chromatography (ASTM 1979). Concentrations of benzene greater than 1 ppm can be measured by direct injection of the water sample into the gas chromatograph (GC). This is the method of choice when the identification of a spill is necessary or when low levels of benzene are present (see Section 11.1.1).

A representative sample is collected in a glass bottle. Analysis is by GC using various columns and detectors described in Section 11.1.1. If the sample concentration is less than 1 ppm, it may be concentrated by evaporation, freeze-out, solvent extraction or adsorption on activated charcoal. Highly concentrated samples may be diluted. Particulate or suspended matter must be removed by centrifugation or membrane filtration. Acidification of the sample will help to dissolve particulate matter. An advantage of the GC method is that in the event of a mixed spill, two or more substances may be separated and analyzed. This method can be combined with mass spectroscopy for positive identification of the sample.

11.3.2 Infrared Spectroscopy (AWWA 1976). Concentrations of 4 to 40 ppm benzene in water can be measured using 1 cm path length cells with a precision of ± 10 percent.

Approximately 1 L of water is collected, the volume determined accurately and the sample acidified with hydrochloric acid. The benzene is extracted using Freon 113[®] (1,1,2-trichloro-1,2,2-trifluoroethane). Recovery is 99 percent. Using matched quartz cells with Freon 113[®] in the reference beam of a double beam IR recording spectrophotometer, the sample is scanned from 3200 cm^{-1} to 2700 cm^{-1} . The advantage of this method over methods that involve heating the sample is that sample loss through volatilization is minimized. This method lacks high sensitivity but is adequate for spills. It is not specific and assumes that the identity of the spill is known.

11.3.3 Gravimetric (AWWA 1976). This method is suitable for concentrations of benzene greater than 10 ppm. The precision is ± 6 percent.

Approximately 1 L of sample is collected, the volume accurately determined and the sample acidified with hydrochloric acid. The benzene is extracted using Freon 113[®] (1,1,2-trichloro-1,2,2-trifluoroethane). Recovery is 99 percent. The Freon is distilled from the extraction flask on a water bath at 70°C. Sample loss may be a problem if the temperature is not carefully controlled. Air is drawn through the flask for the final minute to remove all traces of the Freon 113[®]. The flask is cooled and weighed.

This is a simple and inexpensive method which does not require complex instrumentation. It is not highly sensitive or specific but is adequate for spills of a known substance.

11.4 Qualitative Method for the Detection of Benzene in Water. The water sample is extracted with chloroform and the Friedel-Crafts alkylation reaction is used to identify aromatic hydrocarbons. Anhydrous aluminum chloride (about 100 mg) is placed in a test tube and heated until it sublimes. When it has cooled, a drop of the extract and two drops of chloroform are added with shaking. The appearance of an orange-red colour indicates the presence of an aromatic ring (Owen 1969).

The infrared spectroscopy method discussed in Section 11.3.2 may be used for qualitative identification by observing the presence of absorption bands between 3200 cm^{-1} and 2700 cm^{-1} (AWWA 1976).

11.5 Quantitative Methods for the Detection of Benzene in Soil

11.5.1 Gas Chromatography (NIOSH 1977; ASTM 1979). Concentrations of benzene at the ppm level may be detected using a flame ionization detector. The detection limit may be extended to the ppb level by the use of a photoionization detector or an infrared detector as described in Section 11.1.1.

Approximately 20 g of soil, accurately weighed, are collected in a glass jar and dried by the addition of magnesium sulphate. Freon 113® (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract benzene from the soil. The Freon is distilled from the extraction flask on a water bath at 70°C . Sample loss may be a problem if the temperature is not carefully controlled. Air is drawn through the flask for the final minute to remove all traces of the Freon 113®. The residue is dissolved in carbon disulphide. This is injected into a gas chromatograph equipped with a column and detector as described in Section 11.1.1. This is the method of choice when the identification of a spill is necessary or when low levels of benzene are present.

11.5.2 Infrared Spectroscopy (AWWA 1976). Concentrations of 4 to 40 ppm in soil may be measured using 1 cm path length cells.

Approximately 20 g of soil, accurately weighed, are collected in a glass jar and dried by the addition of magnesium sulphate. Freon 113® (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the benzene from the soil. Using quartz cells with Freon in the reference beam of a double beam IR recording spectrophotometer, the sample is scanned from 3200 cm^{-1} to 2700 cm^{-1} . This is a simple, inexpensive method. It lacks sensitivity but is adequate for spills of a known composition.

11.5.3 Gravimetric (AWWA 1976). This method is used for the detection of concentrations greater than 10 ppm benzene in soil.

Approximately 20 g of soil, accurately weighed, are collected in a glass jar and dried by the addition of magnesium sulphate. Freon 113[®] (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the benzene, then distilled from the extraction flask on a water bath. A temperature of 70°C must be carefully controlled or sample loss will be a problem. Air is drawn through the flask for the final minute. The flask is cooled and weighed. This is a simple, inexpensive method. It lacks sensitivity and specificity, but is adequate for spills of a known composition.

11.6 Qualitative Method for the Detection of Benzene in Soil

The Friedel-Crafts alkylation reaction is used to identify aromatic hydrocarbons. A sample of soil is extracted with Freon 113[®] (1,1,2-trichloro-1,2,2-trifluoroethane) and the Freon evaporated as in Section 11.5.3 above. The residue is taken up in chloroform. Approximately 100 mg of anhydrous aluminum chloride is placed in a test tube and heated until it sublimes. When it has cooled, several drops of the chloroform containing the residue are added with shaking. The appearance of an orange-red colour indicates the presence of a compound containing an aromatic ring (Owen 1969).

The infrared spectroscopy method discussed in Section 11.5.2 may be used for qualitative identification of benzene by observing the presence of absorption bands between 3200 cm^{-1} and 2700 cm^{-1} (AWWA 1976).

12 REFERENCES AND BIBLIOGRAPHY

12.1 References

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand	MMAD	mass median aerodynamic diameter
b.p.	boiling point	MMD	mass median diameter
CC	closed cup	m.p.	melting point
cm	centimetre	MW	molecular weight
CMD	count median diameter	N	newton
COD	chemical oxygen demand	NAS	National Academy of Sciences
conc.	concentration	NFPA	National Fire Protection Association
c.t.	critical temperature	NIOSH	National Institute for Occupational Safety and Health
eV	electron volt		
g	gram		
ha	hectare		
Hg	mercury		
IDLH	immediately dangerous to life and health		
Imp. gal.	imperial gallon	nm	nanometre
in.	inch	o	ortho
J	joule	OC	open cup
kg	kilogram	p	para
kJ	kilojoule	P _c	critical pressure
km	kilometre	PEL	permissible exposure level
kPa	kilopascal	pH	measure of acidity/alkalinity
kt	kilotonne	ppb	parts per billion
L	litre	ppm	parts per million
lb.	pound	P _s	standard pressure
LC ₅₀	lethal concentration fifty	psi	pounds per square inch
LC _{LO}	lethal concentration low	s	second
LD ₅₀	lethal dose fifty	STEL	short-term exposure limit
LD _{LO}	lethal dose low	STIL	short-term inhalation limit
LEL	lower explosive limit	T _c	critical temperature
LFL	lower flammability limit	TC _{LO}	toxic concentration low
m	metre	T _d	decomposition temperature
m	meta	TD _{LO}	toxic dose low
M	molar	TL _m	median tolerance limit
MAC	maximum acceptable concentration	TLV	Threshold Limit Value
max	maximum	T _s	standard temperature
mg	milligram	TWA	time weighted average
MIC	maximum immision concentration	UEL	upper explosive limit
min	minute or minimum	UFL	upper flammability limit
mm	millimetre	VMD	volume mean diameter
		v/v	volume per volume
		w/w	weight per weight
µg	microgram		
µm	micrometre		
°Be	degrees Baumé (density)		

